### Volume 4: Potential Ground and Surface **Water Impacts**

### Chapter 8: Screening Analysis of Potential **Groundwater Resource Impacts from Gasoline Containing Ethanol or MTBE**

Using an Empirically based, Probabilistic Screening Model

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### 8. Screening Analysis of Potential Groundwater Resource Impacts from Gasoline Containing Ethanol or MTBE

Using an Empirically based, Probabilistic Screening Model

### 8.1. Introduction

Although California has implemented an Underground Storage Tank (UST) upgrade program, releases from leaking underground fuel tanks (LUFTs) will continue to be an issue (Giannopoulos, 1999). Moreover, various authors (Chapter 4, Vol. 4 of this report; Malcolm Pirnie, Inc., 1998; Molson *et al.*, 1999; Schirmer *et al.*, 1999; Ulrich, 1999) report that ethanol may lengthen benzene plume lengths due to preferential biodegradation of ethanol. Longer plumes suggest that potentially more public and private drinking water wells in California may be impacted by benzene released from LUFTs.

In this study, we utilized a systems-based approach to estimate the differences in groundwater resource impacts from LUFT releases of benzene, benzene under the influence of ethanol, and methyl tertiary butyl ether (MTBE). Benzene in association with ethanol is the primary focus of this study, because it is a known human carcinogen, and because increased benzene groundwater plumes are predicted. This report examines the potential for benzene to contaminate drinking water sources from future releases of gasoline containing ethanol in contrast to the potential for MTBE to contaminate drinking water sources. MTBE is a possible carcinogen, can affect water quality, has a disagreeable taste and odor at low parts-per-billion (ppb) concentrations, and has been shown as generally recalcitrant in groundwater under *in situ* conditions. This study does not examine the potential for ethanol-only plumes to impact drinking water supplies because ethanol degrades rapidly in groundwater and is expected to have very localized and minor impacts relative to benzene or MTBE.

To estimate the potential future impact of gasoline containing either ethanol or MTBE, we considered some important characteristics of drinking water wells and LUFT sites. These characteristics include:

- The current distribution of the distance to the nearest well from a LUFT site.
- Densities of LUFTs and drinking water wells.
- Past impacts of benzene, toluene, ethyl benzene, and xylenes (BTEX) and MTBE on drinking water wells.

The estimation makes use of probabilistic analytical screening models, using empirically based compliance data collected throughout the state of California. Details of this collection are found in Rempel *et al.* (1996), and the data are described in Dooher (1998).

For chemistry data, locations of wells, LUFT sites, and well yield and construction, we relied on data collected from state and local agencies<sup>1</sup> that has been reviewed and standardized for

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<sup>&</sup>lt;sup>1</sup> The state agencies include information from the State Water Resources Control Board (SWRCB) Leaking Underground Storage Tank Information System (LUSTIS) database (SWRCB, 1999); the California Department of

import into the SWRCB Internet-accessible database, the Geographic Environmental Information Management System (GEIMS)<sup>2</sup>.

### 8.1.1. Methodology

Our estimate of future impacts to public drinking water wells is based on a series of assumptions regarding the spatial distribution of LUFTs that may act as release points, and their proximity to drinking water wells. To compare the potential future impacts to drinking water wells, we developed a baseline impact estimate for benzene without the presence of ethanol (or MTBE). This baseline impact estimate provided a basis for comparing estimated future impacts with MTBE and those associated with benzene under the influence of ethanol.

To estimate the baseline percentage of benzene LUFT-related releases that may impact public drinking water wells over time, we developed a methodology to estimate benzene plume behavior using a Monte Carlo simulation of a one-dimensional advection, three-dimensional (3-D) dispersion equation developed by Cleary and Ungs (1978). The first step in this methodology is to model expected populations of benzene plume lengths without ethanol. Next, we compared the benzene-only plume-length results against measured, historical-case benzene plume lengths to validate the model. Finally, we used the model to develop a population of MTBE plume lengths to be compared against the baseline benzene impacts. Section 8.2. details this methodology and the resulting benzene and MTBE plume length population distributions that we used in this comparative analysis. The samples of benzene plume lengths with ethanol present used for comparison to the baseline were derived from modeling results (McNab et al., 1999b; Vol. 4, Chapter 4 of this report). Figure 8-1 is an example of how this was applied to two sample populations of plume length distributions. We used the difference between benzene plume lengths with and without ethanol as developed in McNab et al. (1999b; Vol. 4, Chapter 4 of this report) as a multiplier for the benzene plume lengths used in this study (Section 8.3.).

We used the three population distributions (benzene without ethanol, benzene with ethanol, and MTBE) to estimate the absolute probability of threat to drinking water wells near LUFT sites. The difference between the probabilities of impact was then used to develop the relative impact threat between benzene with ethanol and MTBE compared against the baseline benzene realizations. Finally, these results are discussed in context to known well BTEX and MTBE detections as found in the CAL-DHS Water Quality Monitoring (WQM) database. Additionally, we examined confounding factors and discussed their potential influences on public- and private-well impacts.

Health Services (CAL-DHS) Water Quality Monitoring (WQM) and the Permitting, Inspection, Compliance, Monitoring, and Evaluation (PICME) databases (CAL-DHS, 1999a,b); and the California Department of Water Resources (CAL-DWR) EXTERRA database (CAL-DWR, 1997). Yield and well construction data was obtained from local agencies including the Santa Clara Valley Water District (SCVWD, 1999) and Orange County Water District (OCWD, 1999).

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<sup>&</sup>lt;sup>2</sup> GEIMS is a water resources and contaminant database created for the SWRCB to manage LUFT sites. It is accessible through an Internet Geographic Information System (GIS) interface, GeoTracker, at <a href="http://geotracker.llnl.gov">http://geotracker.llnl.gov</a>.

# **8.2.** Forecasting Benzene (Degrading) and MTBE (Nondegrading) Fuel Hydrocarbon Plume Behavior

#### 8.2.1. Introduction

Dooher (1998) discussed the importance of developing models appropriate to the available data when assessing situations of high uncertainty. Because the goal of any model is to predict the future or to fill in the gaps where not enough information is available, a modeling approach should attempt to develop confidence intervals for future predictions or fill in these gaps. These predictions forecast at some point in space what may occur now, five, ten, or 100 years in the future. In this screening model, these forecasts are used for developing "probability domains" to describe the likely area of movement of fuel hydrocarbon (FHC) plumes in the subsurface. The analysis of McNab *et al.* (1999b; Vol. 4, Chapter 4 of this report) applies a similar approach to the assessment of benzene plumes affected by ethanol.

This section provides the details for three major methodologies used in forecasting resource impacts associated with the use of ethanol as a fuel oxygenate:

- A comparison of forecast benzene plume lengths to plume lengths derived through various methodologies (Dooher, 1998), in order to validate the general model.
- An examination of the time history of degrading chemicals (such as benzene), its plume lengths, growth rates, and recedence rates.
- An examination of the time history of nondegrading chemicals, (such as MBTE), their plume lengths, growth rates, and recedence rates.

These plume lengths derived here for a large population of sites are then used as the basis to develop the probability of well impacts in California from benzene with and without ethanol and from MTBE.

The following discussion addresses two important elements of the evaluation of plume impacts to groundwater resources. The first examines the development of an underlying conceptual model of a plume, and the second applies Monte Carlo analysis to the conceptual model.

### 8.2.2. Conceptual Model of a Plume

A plume in its most abstract form moves downgradient, dispersing normally to the primary gradient direction in two directions. Figure 8-2 shows the conceptualization of the three-dimensional case. The greatest spread takes place horizontally in the primary direction of groundwater flow, with a lesser lateral and vertical transverse spread due to dispersion and smearing through zones of relatively higher conductivity (Gelhar *et al.*, 1985).

For advection-dispersion and degradation in the subsurface, due to the heterogeneities present, an "exact" solution for the transport of a contaminant is possible only when these heterogeneities are accounted for—typically in some form of numerical modeling. This section examines a probabilistic approach, wherein a mathematically exact or approximate analytical solution is derived for three dimensions and used to produce a series of probabilistic realizations by applying a Monte Carlo methodology. Although analytical solutions to the advective-dispersion solute transport equation lack the general flexibility offered by numerical methods,

they may serve as probability distribution models for contaminant concentrations as a function of space and time in many situations. Analytical approaches are particularly well suited for application of Monte Carlo techniques because of the speed of solution.

Monte Carlo analyses allow uncertainties in governing parameters (for example, groundwater velocity, contaminant degradation rate, source attenuation rate) to be addressed as assumed probability distributions for input to the model. The analytical solutions typically assume a homogeneous environment in which the groundwater flow is uniform in one direction. Probability distribution functions for the various parameters are placed into the models, and upper and lower confidence intervals are developed. When compared to actual environmental measurements, this method leads to a greater understanding of the uncertainty of the contaminant-plume movement relative to the variability of the subsurface.

The descriptive equation of transport for a uni-directional flow, three-dimensional plume with sorption and decay is the advection-dispersion equation

$$R\frac{\partial C}{\partial t} = D_X \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} - v_X \frac{\partial C}{\partial x} - \lambda RC \tag{8-1}$$

There are multiple analytical solutions that can be used with Equation (8-1), both for transient and nontransient situations. Many of these are discussed by Bear (1972, 1979), Wilson and Miller (1978), Cleary and Ungs (1978), van Genuchten and Alves (1982), and Wexler (1992). The 3-D solution to the Cleary and Ungs (1978) model of the form:

$$C = f\left(x, y, z, t, v, D_x, D_y, D_z, R, \lambda, \gamma\right)$$
(8-2)

is used to as the plume probability domain. The specifics of the solution are found in Appendix A. Table 8-1 shows the variables used in the solution.

### 8.2.3. Monte Carlo Analysis

When used in conjunction with analytical models, Monte Carlo analyses of contaminant transport involves running multiple simulations (realizations) in which input parameters are allowed to vary in accordance with assumed probability distributions. The output of the Monte Carlo analyses is forecast frequency distributions of variables of interest (that is, plume length, plume growth, and recedence rate). Thus, the probability of a plume reaching a certain length or achieving a certain growth rate may be quantified (along with associated uncertainties).

For the first analyses, we conducted 4000 Monte Carlo realizations on two different source populations using the analytical solution (Equation A-4a) of Cleary and Ungs (1978). These realizations were used to forecast the 1 part-per-billion (ppb) contour-interval hydrocarbon-plume lengths and associated growth rates. Probability distributions of governing parameters were generated using literature sources, best professional judgment (BPJ), and data developed in Dooher (1998) (shown in Table 8-2). Plume-length distributions developed are then compared to the resultant Monte Carlo forecasts.

### 8.2.4. Results of Plume Length Forecasts

### 8.2.4.1. Degrading Plumes

**8.2.4.1.1.** Plume Lengths. Forecast cumulative distribution functions of benzene plume lengths are generated, as defined by the distance from the source (x = 0) to the 1-ppb contour interval along the plume longitudinal axis. These were created using the three-dimensional model described earlier, applying two different input distributions to simulate free product (FP) and non-free-product (NFP) sources. The only change in variables between them is the concentration distribution. FP concentrations are based on observed distributions on sites that have recorded free product, while the dissolved-concentration distribution is representative of sites with no observed free product.

Staff of the State Water Resources Control Board (SWRCB) drew over 500 plumes (some are plumes drawn at several periods on the same site) using BPJ. (BPJ is defined as manually viewing the spatial distribution of concentrations and the groundwater gradient direction.) Concentration contours are then drawn on a site map, and the plume length measured. The measure of the plume length across its long axis is C to C, "contour to contour." Max to C is the measurement of the plume length across its long axis from the point of maximally found concentration. Typically measured were the 10-ppb and 1-ppb contours for benzene. Contours were drawn to be as conservative as possible, using historical data to fill in gaps of missing groundwater chemistry concentrations. The length was estimated using the highest historical groundwater concentrations. We used these lengths as a comparison in the following analyses. Figure 8-3 shows BPJ plume lengths<sup>3</sup> correlated against maximum site concentration.

It is immediately apparent that there is an effective "exclusion zone" in which, for a given concentration, there are no plumes greater than a certain length, implying the existence of natural constraints imposed by the physics of the subsurface transport phenomena. These constraints are likely to be the maximum velocity and the minimum degradation rate. For higher maximum benzene concentrations above 5000 ppb<sup>4</sup>, the plume lengths begin to fall out of the exclusion zone. Figure 8-4 shows the same figure with log-transformed plume lengths, where the "exclusion zone" still holds for larger plume lengths. McNab *et al.* (1999a) found a very similar trend for chlorinated volatile organic compounds but with much exaggerated plume lengths.

Figure 8-5 compares this distribution with the distributions developed using BPJ and through the nonparametric approach found in Dooher (1998). To create uniformity, all plume lengths less than 25 ft were deleted because these small plumes would not be typically detected at the sampling distances characterized by monitoring well spacing. Though there is a definite scatter of the cumulative distributions, the same trends and ranges are very apparent. The Monte Carlogenerated plumes fall nicely into the center of the range and, more importantly, characterize what would be the 95<sup>th</sup>-percentile confidence level associated with a plume forecast.

**8.2.4.1.2. Plume-growth Rates.** For the population evaluated, plumes were forecast over time, starting at Year 1, and then at 5-year intervals starting at Year 5 after the release. Figure 8-6 shows the cumulative distributions of plume lengths for Years 1, 5, 20, 30, 40, 50, 60,

<sup>&</sup>lt;sup>3</sup> As developed by Rick Rempel of the SWRCB (Dooher, 1998).

<sup>&</sup>lt;sup>4</sup> Dooher (1998) found that concentrations at these levels are highly correlated with "free product" or floating nonaqueous phase liquid (NAPL) product.

70, 80, 90, and 100. Some plumes literally explode into existence and can then rapidly decline, whereas others grow gradually and degrade gradually. Because a large percentage of the plumes expires over time, at Year 100 almost 70% of all plumes have decayed. Figure 8-7 shows the percentile plume lengths over time. The 95<sup>th</sup> percentile results show a peak at ten years at approximately 1600 ft, declining to 250 ft by Year 100. Figure 8-8 shows the same results with the plume length on a log scale. Figure 8-9 shows a sampling of various generated degrading plumes, from which the populations shown in Figures 8-6, 8-7, and 8-8 were developed.

Figure 8-10 shows the year interval at which the plume population reaches a peak. After 50 years, almost all plumes will have reached a maximum peak length. Figure 8-11 shows a box distribution of the plume lengths at the time of maximum extent for the populations in Figure 8-10. Median plume length ranges from 100 to 1000 ft with a slight trend upwards as time progresses as expected. Plumes that are still growing after 50 years must have very small degradation rates.

Figure 8-12 shows the cumulative distributions of plume-growth rates for various intervals of time. The maximum growth rate typically takes place in the first year, diminishing over time to a maximum of 0.1 ft/day for the 40- to 100-year range. For the plume-length decay rate, the initial decay is almost at its peak, peaking in the five- to ten-year range and then dropping off. The differences in the distributions are no more than a few tenths of a foot per day.

Figures 8-13 and 8-14 show the time required for plumes to extinguish. Initial surges of plumes vanish entirely within one year (approximately 10%). These would be associated with small releases. After this initial surge, there is an upward trend of time necessary to reach zero length, peaking for both FP and NFP populations at around 50 years. Figure 8-14 shows the maximum plume length associated with the time necessary to reach zero. The median for those plumes taking less than 20 years to reach zero length is generally small—no more than 20 ft. The median plume length tends to stabilize around 80 ft as longer times are necessary to reach zero-plume length.

### 8.2.4.2. Nondegrading Plumes

- **8.2.4.2.1. Plume Lengths.** Nondegrading plumes behave very differently from those where source depletion and overall degradation occur. Figure 8-15 shows the cumulative distributions of plume lengths for (nondegrading) plumes with a constant source. A small percentage of simulations result in zero-length plumes; all are associated with low initial concentrations and rapid velocities. As time progresses, however, the plume distribution approaches an asymptote with the 95<sup>th</sup> percentile approaching approximately 15,000 ft (3 mi) in length. In contrast to the degrading plume sites where, on a year-by-year basis, an increasing number of sites reach a zero-plume length, no such effect occurs here. It is likely that sites exist where groundwater has been impacted but due to local conditions (such as a low relative flux rate from the vadose zone in combination with a high advective groundwater flow rate), the effect is minimal.
- **8.2.4.2.2. Plume-growth Rates.** Figures 8-16, 8-17, and 8-18 show the plume length trends over time for various percentile intervals. Figures 8-16 and 8-17 show a close-up of the lower percentile ranges as well as the total range. Very few of the percentiles have reached steady state. Figure 8-18 shows this more explicitly. Most of the percentiles show a slowly declining rate of growth trend on a log-log scale, with only the lowest percentiles showing any

deviation downward. These lengths are overly conservative because there is no source attenuation, which would occur in reality. Figure 8-19 shows a sampling of the various plume lengths from which the cumulative distributions are developed. Further work is being performed to assess the general source attenuation rate for MTBE sites.

Figure 8-20 shows the year at which the simulated plumes reach steady state for nondegrading plumes. By Year 100, 46% of the simulations have not reached steady state. Figure 8-21 shows the growth rates for FP and NFP plumes after 100 years. The 95<sup>th</sup> percentile is still approximately 60 ft/y. Figures 8-22 and 8-23 show growth rates at various time intervals for FP and NFP. Initial growth rates are much higher than those found in degrading plumes and stay high. This is in contrast to the growth rates of degrading sites that at Year 100 are an order of magnitude less in size than nondegrading plumes.

# 8.3. Comparison of Potential Future Impacts Associated with Benzene Either in the Presence of Ethanol or in the Presence of MTBE

## **8.3.1.** Location Relationship between LUFT Sites and Public Drinking Water Wells

The potential threat from a LUFT site release to a well depends on the relative locations of nearby drinking water wells and the density (or count) of LUFT sites near the well. Figure 8-24 shows the minimum separation distance of LUFT sites from public drinking water wells and vice-versa<sup>5</sup>. Because there are many more LUFT sites than drinking water wells (approximately 35,000 LUFTs versus approximately 15,000 wells), 32% of LUFT sites are estimated to be within 2000 ft of a drinking water well, while 38% of well locations are estimated to be within 2000 ft of a LUFT site.

Figures 8-25 and 8-26 show density distributions as a percentage of LUFT sites and public drinking water wells within a range of distances. These graphs show the percentage of wells (or LUFT sites) and a count of the number of LUFT sites (or wells) within a given distance. For example, in Figure 8-25, approximately 45% of wells have at least one LUFT site within 2500 ft, and 31% of wells have at least two LUFT sites within 2500 ft.

## **8.3.2.** Screening Model Estimate of the Probability of Future Impacts to Public Drinking Water Wells from LUFT Sites

### 8.3.2.1. Probability of a LUFT Site Impacting the Closest Well

To assess the potential impact of LUFT releases of gasoline containing either ethanol or MTBE, we considered the distribution of the separation distances between known LUFT sites and drinking water wells (Figure 8-24). The probability distributions of plume lengths for MTBE and benzene (Figures 8-6 and 8-15) and for the increased lengths for benzene with ethanol may be compared against distances between LUFT sites and drinking water wells as a function of time since plume release. The distance between the LUFT site (the plume source)

<sup>&</sup>lt;sup>5</sup> The determination of the locations of LUFT sites and public drinking water wells are discussed in Dooher and Happel (1999) and were originally found in SWRCB (1999) and CAL-DHS (1999b).

and the nearest drinking water well is related to the probability that a plume may migrate that distance. The probability of impact from benzene, benzene under the influence of ethanol, or MTBE for each LUFT/well distance may then be determined. It is then possible to compare the absolute and relative probabilities<sup>6</sup> of increased threat to the closest well adjacent to a given LUFT.

In developing these probabilities of impact, we assumed that the plume is heading downgradient toward the drinking water well. This conservative assumption is made because the direction of groundwater flow for these sites are unknown. Typically, LUFT sites are randomly situated in relation to drinking water wells; it is likely that the actual impacts may be much less. These impact probabilities for MTBE are conservative in that they assume no source or dissolved plume attenuation; however, they do allow the determination of relative changes in the probability over time. Section 8.5. discusses further how various uncertainties can affect these estimates.

Figures 8-27 and 8-28 show absolute probability of threat for benzene, with and without ethanol. Intervals as shown are for 1-, 5-, 10-, 15-, 50-, and 100-year cumulative probabilities of threat. The absolute probability of threat for benzene under the influence of ethanol, as seen in Figure 8-28, increases substantially. For the one-year interval for at least 10% of sites, the absolute probability of threat more than doubles. Similarly, the five-year interval, which shows the maximal predicted threat probability, also increase by a factor of two, to approximately 28%.

Figure 8-29 and 8-30 show the absolute probabilities of threat in detail. Twenty-five years after the benzene release, in both cases, the plume has returned to approximately the same probability distribution as Year 1. Maximal probabilities of threat occur in the five- to ten-year range. The decline of benzene over this timeframe (as seen in Section 8.2.) is due primarily to the attenuation of benzene sources and the degradation of the plume. This attenuation and degradation cause the benzene plume to slowly recede over time. Source attenuation rates are based on the results of field compliance data as stated in Dooher (1998). Degradation rates are based on results obtained from the same source as well as published data. In the case of MTBE, Figure 8-31 shows the total range of the LUFT-site populations and probabilities, as do Figures 8-27 and 8-28. In contrast, MTBE continues to have an increasing absolute probability of impacting wells for as long as 100 years although at this point it is reaching an asymptotic limit.

Of greater interest is Figure 8-32, which shows the relative change in probability between the absolute probabilities of Figures 8-27 and 8-28. The differences in these two distributions were used. We assumed that the benzene probabilities are the baseline case because benzene has been a ubiquitous contaminant at LUFT sites for many years. The important factor, therefore, is the *change* in the probability of impact to a drinking water well. The results show an initial increase in impact probability of 18% by the fifth year for a small percentage of sites (less than 3%). The average impact is an increase of approximately 10%. Examining the temporal change in relative probability (Figure 8-33), the greatest increase is in the first five years, dropping to a negative

<sup>&</sup>lt;sup>6</sup> The meaning of "absolute probability" is different from a statement that this is the actual probability that the well will be impacted, as there are many additional confounding factors that are not taken into account in this simple two-dimensional exercise. It is the relative probability that is of the greatest importance here. See Section 8.4. for a discussion of these.

rate change thereafter (as can be seen from the overall trends). The average change is approximately 2.5% in the first five years.

Figure 8-34 shows the temporal trend of the change in absolute probability for MTBE. The first five years show the greatest growth patterns, reaching a maximum of approximately 24%. This growth continues in the five- to ten-year range, where the relative change is still 10%, dropping to 5% for the five- to ten-year range, and to 2.5% for the 20- to 25-year range. This indicates that unmanaged MTBE sources can continue to act as a hazard for long periods into the future. Current work is attempting to ascertain rates of source attenuation that can be applied to MTBE; earlier work (reported in Happel *et al.*, 1999) shows a marked difference when a source-attenuation rate similar to benzene is used.

#### 8.3.2.2. Probability of a LUFT Site Impacting Many Surrounding Wells

Basic probability calculus (de Morgan's rule) (Ang and Tang, 1975) can be used to estimate an absolute and relative probability of threat to drinking water wells. This approach assumes independence of the well locations. For multiple wells in a given LUFT-site area, the probability of impacting any well in the area is given by de Morgan's rule:

$$P\{E_1 \cup E_2 \cup \dots \cup E_n\} = 1 - P\{\overline{E_1 \cup E_2 \cup \dots \cup E_n}\}$$

$$= 1 - P\{\overline{E_1}\overline{E_2}...\overline{E_n}\}$$
(8-3)

where  $E_i$  is the event probability, and  $\overline{E}_i$  is the complementary form of the event probability, or  $\overline{E}_i = 1 - E_i$ . An assumption of independence for the surrounding wells is not exactly correct, as their spatial position is approximately known. Known locations turns the problem into one where there is dependence (that is, if the plume moves in a direction where three wells are located, the probability of impact of a further well necessitates the impact of the closer well). A sensitivity study of this dependence is under development.

As an example, we assumed that the probability of a plume reaching a well 1000 ft distant would be 0.25, and for a well 2000 ft distant, it would be 0.10. Assuming a well at 1000 ft and one at 2000 ft, the total probability of impact threat to either well is

$$3\mathfrak{P} = 0.5 \quad \text{(1-8)} \quad \text{(2-4)} \quad \text{(3.4)} \quad \text{(3.4$$

Taking the example further, using this screening approach the probability of threat to any of six wells, all at a distance of 1000 ft, would be 82.2%.

Using information in the GEIMS database, the above approach to estimating the probability of impact from a single LUFT was applied to all known open LUFT sites and active drinking water wells in California. Drinking water wells that exceeded a distance of 30,000 ft from a given LUFT were excluded in this analysis<sup>7</sup>. In all, we evaluated 15,525 open-case LUFT sites with geocodable addresses.

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<sup>&</sup>lt;sup>7</sup> This is due to the almost nonexistent probability of a plume reaching this distance (based on the modeling).

Figure 8-35 shows the modeled absolute probability over a 100-year time span for the 30% of LUFT sites in California where benzene may threaten to impact a well. Potential impacts for benzene with and without ethanol are shown. For example, the addition of ethanol increases the initial impact threat difference by over 20% for up to 10% of LUFT sites. Thereafter, this change in total probability decreases. For at least 20% of LUFT sites, the increased difference in probability is at least approximately 14%. For 30% or more of sites, the change in total threat probability is at least 7%. All these maxima occur in the five- to ten-year timeframe, much as we saw with the LUFT site and the single well. The decrease is due to benzene-source attenuation and overall degradation.

The relative change, as stated above, is of primary import. Given the addition of ethanol, a majority of LUFT sites will show relatively little additional chance of impacting nearby wells. Those sites that are already at a high absolute probability of threat will increase dramatically up to 20%, or approximately 1550 wells.

Figure 8-36 shows the estimated absolute probability of a given percentage of LUFT sites in California where MTBE may threaten to impact a well across a 100-year time span. For example, 10% of the sites have a 30% probability of threat in the first five years, increasing again by an additional 15% during Years 5 to 10. Because the modeled MTBE plumes are assumed to be nondegrading, they continue to expand and represent increasing threats with time. This expansion and increasing threat are in contrast to the benzene sites that have peak potential impact threat approximately seven years after release, after which point they begin to decrease in threat (Figure 8-35).

Figure 8-37 shows the relative probability increase between sites impacted by benzene alone and those sites where benzene is under the influence of ethanol, for approximately 5% of sites (the 95<sup>th</sup> percentile as shown on the figure). Benzene is again stated to be the baseline for comparison. The result of this comparative estimate is that there is an approximately 20% maximum predicted increase in public drinking water well impacts for benzene with ethanol in the five- to ten-year frame. This relative rate of impact begins to decrease thereafter.

An examination of the relative change in probability of MTBE impact reveals a significantly increased chance of impacting a well. At about seven years, the probability of impact for MTBE and benzene under the influence of ethanol is about the same. The major difference between MTBE and benzene under the influence of ethanol is that the probability of MTBE impact continues to increase with time as MTBE plumes continue to grow. Figure 8-37 shows the maximum expected change in well impacts, using benzene without ethanol as a baseline. By Year 10, an MTBE release has an increased probability of impact of 45% over the baseline benzene impacts, or more than twice the threat that benzene in the presence of ethanol represents.

It is important to note that all quantitative findings, such as the estimated relative probability of impacts, reflect probabilistic modeling results and are highly sensitive to the underlying probability distributions and simplifying assumptions for the various modeling inputs. This comparative analysis is intended as a screening tool and is not intended to provide formal quantitative predictive values that could be used for detailed resource planning purposes. Further work is being performed to assess the absolute and relative probabilities with known maximum concentrations of benzene and MTBE. These results should be significantly less than those shown here and will be of significantly greater use.

### **8.4. Important Uncertainty Considerations**

To estimate the impact to public drinking water wells, we assumed that the modeled increase in probability due to a change in gasoline composition could be based on what is current knowledge of benzene impacts. However, some important uncertainties are inherent in the use of the known benzene impacts:

- Many wells had not been tested as of January 1995 (approximately 50% of those wells had been sampled more than once). That five-year period may have resulted in a low concentration impact that, upon mixing with other water sources, would not be noticed. The same holds true for MTBE.
- The statistical population used as a baseline for MTBE impacts is those wells that are required by CAL-DHS<sup>8</sup> to sample for nonregulated chemicals or secondary maximum contaminant levels (MCLs) (such as MTBE). This decrease in sampling frequency may increase the possibility that benzene or MTBE could reach a drinking water well undetected.
- Although most LUFT data collected are two-dimensional in nature, the problem is in reality three-dimensional. Wells are screened at different depth intervals across the state, depending on the type of water usage and the local groundwater depth. Factors that introduce uncertainty include vertical flows that occur from well use (which could increase the vertical transport downward), artesian aquifers (that cause upward gradients), and confining layers of low hydraulic conductivity that act to prevent downward flow, upwards or downwards. Although hydrocarbons, which are light nonaqueous phase liquids (LNAPLs), are referred to as "neutrally buoyant" in the dissolved phase, rainfall can also act to drive the plume downward.

### 8.4.1. Location Accuracy of Drinking Water Wells and LUFT Sites

An important uncertainty in this analysis and in any future assessment of potential impacts is the accuracy of locations of public drinking water wells in the CAL-DHS (1999b) PICME database. Dooher and Happel (1999) demonstrated a technique to improve significantly the location accuracy of public drinking water wells. The improved location data are used in this analysis. CAL-DHS, in cooperation with the SWRCB, plans to expedite finding accurate locations of wells in close proximity to LUFTs by November 2000 in order to comply with Senate Bill 989 (1999).

Ascertaining the locations of LUFT sites and operating UST sites within the pilot areas and within the state is much simpler than locating wells accurately. Because LUFTs and USTs are specific, large facilities, their locations can be determined with moderate to high accuracy based on addresses of commercial sites. LUFT sites used in this study are based on ETAK<sup>9</sup> geocoding, which returns an approximate location and associated accuracy based on street addresses. Geocoding finds latitude and longitude of street addresses using an electronic database of streets

<sup>&</sup>lt;sup>8</sup> Excluded from this population are 3859 public water systems that are considered to be transient noncommunity (TNC) systems (e.g., restaurants, campgrounds). These TNC systems are not required to monitor for unregulated chemicals or chemicals with secondary MCLs.

<sup>&</sup>lt;sup>9</sup> Available at < < http://www.etak.com/>.

and returns a qualifier stating the source of the position. Dooher and Happel (1999) examine the accuracy of geocoding.

Potential problems in geocoding are based more on poor LUFT site and UST facility address data. The SWRCB, in cooperation with Regional Water Quality Control Boards and local permitting agencies, is currently addressing this problem by reconciling local and state databases within the GEIMS database.

### **8.4.2.** Sampling Frequency and Impact Rates of Public Drinking Water Wells and LUFT Sites

Because our estimate indicates that the use of ethanol as a fuel oxygenate may be expected to increase drinking water well impacts as much as 20%, routine monitoring of public and private drinking water wells would be an important step to identifying actual impacts. Figure 8-38 shows the first and most recent sampling-date distributions for 10,972 drinking water sources that have been tested for benzene <sup>10</sup> (CAL-DHS, 1999b). Only those wells that have had multiple sampling are included in this graph. The reported, first-time sampling rate of approximately 1800 sources/year decreased substantially in 1987 to a reported rate of approximately 450 sources/year. This rate is likely due to new wells annually created around the state and reflects initial sampling. In 1999, the sampling-event rate for many of these wells substantially increased. However, a large percentage (40%) of wells has not been sampled or reported as sampled in eight years. It is, thus, not known if there have been any well impacts for this percentage of the population. For MTBE, most sampling has taken place since January 1996, approximately the same time as the first reported impact to Santa Monica's well fields.

In estimating the impact to public drinking water wells, we assumed that the modeled increase in probability due to a change in gasoline composition can be based on the current detection rate. Variations in that detection rate may have a direct impact on the estimate of future impacts.

Figure 8-39 shows the cumulative distribution of time between samples and the average time between samples. The average time between samples is conservative, because "two samples over 10 days" would result in an artificially high sampling rate. In the past year, 10% more wells—a large increase—have been sampled for BTEX. Only 50% of the wells sampled have been sampled more than once. The above results point to an uncertainty in the baseline "detection rate" of BTEX and MTBE in wells around California; therefore, there is inherent uncertainty in the exact estimate of impacted wells.

Appendix B summarizes the results of the routine testing of public water sources throughout California. Tables 8-3 to 8-5 show the yearly count of tested public water sources throughout California. Tables 8-6 to 8-8 show the same counts for sources reporting BTEX and MTBE detections. Overall, the average yearly benzene source detection rate is under 0.35%, as seen in Table 8-9 (also seen as Figure 8-40). Both toluene and total xylenes have a higher rate, 0.53%

requested LPAs to provide their MTBE detection data. These data are included as they are received from the LPAs.

<sup>&</sup>lt;sup>10</sup> It should be noted that these are the numbers reported to CAL-DHS and may not accurately reflect the true sampling frequencies. Almost half (2285) of the 4681 public water systems are small systems and nontransient noncommunity systems regulated by local primary agencies (LPAs), designations given to 34 of California's 58 counties. Data from LPA-regulated systems are not required to be submitted to CAL-DHS. In July 1998, CAL-DHS

and 0.36% respectively. MTBE shows a 1.17% yearly detection rate, much higher than any of the BTEX constituents alone, although similar to the combined BTEX detection rate (1.15%). BTEX and MTBE have a combined water source detection rate of 1.75%. The total detection rate for BTEX and MTBE, as of 1999 (Table 8-10) shows a 0.68% detection for benzene alone, 1.64% for toluene, 1.0% for the xylenes, and 0.62 for ethylbenzene. MTBE, which has not had as many sources tested (approximately 42.3%) and which has only been tested for (and used) recently, has already almost equaled the cumulative yearly detections of toluene, at 1.55%. The combined cumulative detection rate of BTEX is 2.85% and BTEX with MTBE is 3.35%. Finally, the change in detections are seen in Table 8-11. Figure 8-41 shows these trends in a better format, but it can be seen that the average change in detection for MTBE is higher, by 25%, then the change in benzene detections. The overall change in detection trends for BTEX is 6.6%, and with MTBE included, 8.3%.

### 8.4.3. Comparisons of Well BTEX/MTBE Detection Levels, Well Construction, Well Yield, and Groundwater Levels

Figure 8-42 shows a cumulative distribution of maximum concentrations as found in public drinking water wells. These concentrations are orders of magnitudes less than what is observed typically at LUFT sites. If ethanol is added to gasoline, it will likely have a similar effect on the entire range of BTEX components. The levels observed may rise as a result of ethanol's addition to unknown but higher levels.

Figure 8-43 shows the depth to the top of the screen interval for various well types found throughout California. Municipal (public) wells are generally deeper than domestic wells. The median depth for domestic wells, based on selected CAL-DWR records and a more complete database obtained (Dooher and Happel, 1999) from the Santa Clara Valley Water District (SCVWD, 1999) shows a range of 75 to 100 ft. The median for SCVWD and from data collected from the public wells of the Orange County Water District (OCWD, 1999) shows a median that is more wide ranging—from 175 to 350 ft. This range is probably characteristic of depth to top of screen interval for California groundwater, the depth of which is in general deeper in southern California. The CAL-DWR and SCVWD data are from northern California.

Figure 8-43 also shows the cumulative distribution of the top of the screen depth for MTBE-impacted wells across California. It is similar to the SCVWD public wells and deeper than the private well distribution, implying that the depth of private wells may not be sufficient protection against impact.

Of importance in determining concentration levels in wells are both the well yield and the plume concentration that the well takes in. As an example, the Santa Monica Arcadia wells were found to have maximum MTBE levels of 19.6 ppb and 86.5 ppb for average monthly well yields of 7.1 and 13 million gal, respectively (CAL-DHS, 1999a). These levels represent the 85<sup>th</sup> and 95<sup>th</sup> percentiles of the distribution of known MTBE impacts to public wells. The result of performing a simple mass balance gives the actual MTBE levels (on a monthly basis) of 0.14 and 1.13 gal, respectively. Figure 8-44 shows the well yields as collected from SCVWD (1999). The Arcadia wells represent the 84<sup>rd</sup> and 89<sup>th</sup> percentiles of the well yields as found in that database. Private well yields are much less; these are also shown in Figure 8-44.

Figure 8-45 shows the correlation of the depth to top of well screen and the maximum depth to groundwater, based on CAL-DWR records, for the set of private wells found in Figure 8-43.

Where the points lie above the line, the groundwater level is below the top of the well screen, leaving the well more vulnerable to contaminants that come from the surface. Twenty percent of the wells have top of screen intervals that are greater than the groundwater depth. An additional 20% of the maximum groundwater level in the wells are within 20 ft of the top of the screened interval. Various studies have shown the intrinsic vulnerability of domestic wells to surface contamination (specific vulnerability). Details of these studies are found in Dooher (1999).

It is apparent that in public wells, any combination of concentration and yield is possible (that is, low concentrations, low yields; high concentrations, high yields). The Santa Monica Arcadia wells represent the near maximum yield and impacted concentrations seen in California and are, therefore, near the upper limit of what is known to be possible. Little is known concerning the levels of concentrations as seen in private wells. It is known that a private well in Glennville, California, reported MTBE concentrations at the 20,000-ppb level in a fractured rock environment. There were other concerns with this, however, including impacts of coliform and nitrates, as well as *E. coli* in other nearby private wells. Little is known concerning actual impacts to private wells, and more work must be performed to assess that population.

### 8.4.4. Vulnerability of Private Drinking Water Wells

What is not reflected in the screening analysis of potential impacts to public wells are the approximately 1.3 million individuals in California who rely on private drinking water wells as their primary source of water. According to 1990 United State census data, 464,621 California households use some kind of private well US Census, 1992a). Although the locations of these are not exactly known, U.S. census data do provide the information to determine the densities of private wells (see Figure 8-46) from which the relative specific vulnerability of these private wells may be determined<sup>11</sup>, as seen in Figure 8-47. Some local agencies possess databases or listings of private wells; due to privacy considerations, this information is not generally available.

Few compendiums have been issued that look in detail at LUFT sites that have impacted wells, nor the reason for those impacts. In 1995, 55 water-supply wells in the jurisdiction of the Central Valley Regional Water Quality Control Board (CVRWQCB) were reportedly affected by BTEX. The SWRCB reviewed 36 LUFT case files (Rempel, 1995) on those wells and found that unreasonable impairment of actual beneficial uses by benzene from LUFT sites is rare. Of the 55 wells reviewed, only 25 could be reasonably attributed to 19 LUFT sites out of the 5871 sites then reported in the LUSTIS database. Seven of these sites were located in fractured rock and impacted nine water wells, with six of these being onsite wells. The remaining 12 LUFT sites were located in alluvial soils and affected 16 supply wells, five of which were onsite wells. In all cases, the affected wells were less than 200 ft away from the LUFT. Twenty-four of the 25 affected wells were private, domestic wells. The review also found that 11 of the 24 affected private, domestic water-supply wells were shallow, onsite wells at the LUFT site itself. Many of them were described as "hand-dug" and probably had not been completed to current drinking water well specifications. The review concluded that the LUFT potential impacts to groundwater resources should be evaluated based on the proximity and the construction of water-supply wells within a few hundred feet of a LUFT site.

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<sup>&</sup>lt;sup>11</sup> The methodology used to determine this is described in Dooher (1998).

This evaluation was performed prior to the use of MTBE in gasoline, and there are now several hundred well-affected LUFT sites reported in LUSTIS. These sites should be re-examined for detection of MTBE. Additionally, examination of MTBE-impacted public wells may uncover trends or weaknesses in current regulatory oversight that require correction.

#### 8.5. Conclusions

In conclusion, we used a distance approach combined with known impact probabilities and estimated plume lengths to compare the probabilities of threat from LUFT benzene releases (with or without ethanol), or MTBE, impacting drinking water wells in California. This method provides an important advantage because it provides comparative estimates of potential future impacts between MTBE and benzene in the presence of ethanol. The methodology described herein can act as a screening-level approach to identify highly vulnerable areas. The identification of such areas would then be based not only on a single site, but also on multiple sites. The methodology also provides a probability factor for assessing the degradation of the resource in a specific area using a summation of sites.

This method is based on the assumption that only one major variable, plume length, will change as a result of the addition of ethanol to gasoline. All other variables, such as well depth, yield, and locations will stay the same. Therefore, we can use the benzene without ethanol as a baseline on which to assess the changes in detections.

Based on the results of our analysis, an approximate 20% peak relative difference in public drinking water wells impacted by benzene was estimated if MTBE is replaced by ethanol, when compared to benzene alone. This relative increase in public drinking water well impacts is estimated to decline from this peak by ten years after the initial release. However, the estimated potential future increase in public wells impacted by MTBE is significantly higher if MTBE remains the primary fuel oxygenate. By the conclusion of the first ten-year period, estimated MTBE well impacts increase by as much as a 45% difference form the baseline, and continue to increase thereafter. This analysis is very conservative, especially with MTBE. Known concentration levels at LUFT sites were not used in the analysis because only a limited number of LUST sites have a known concentration associated with them. A comparative analysis is underway to evaluate the difference between the above analysis and that of the more limited population.

This approach may be subject to misinterpretations. Because we are examining first an absolute probability, there is a concern that the absolute probability can be taken out of context. It is important that the relative probabilities be used, using the benzene-alone distributions as the baseline.

The evaluation of known detection levels in public water sources as discussed in Section 8.4.2, is to provided some perspective to the magnitude of benzene or MTBE impacts in the past. Overall, the average yearly public drinking water source benzene detection rate is under 0.35%. Both toluene and total xylenes have a higher rate, 0.53% and 0.36%, respectively. MTBE shows a 1.17% yearly detection rate—much higher than any of the BTEX constituents alone—although similar to the combined BTEX detection rate (1.15%). Currently, benzene shows a fairly constant detection rate over time, with a slight downward trend when yearly rates are compared. The use of ethanol as a fuel oxygenate would likely increase this detection rate which may stabilize at some higher level. MTBE shows definite upward detection trends; its continued use

could, based on the trend results, result in more detections in water sources than benzene within the foreseeable future.

Based on the results of this preliminary evaluation, the following are recommended:

- Modeling based on detailed site-specific information is needed. Because the results of these estimates are largely dependent on the input parameter probability distributions, historical-case data that better constrain the uncertainty in these probability distributions will improve the predictive capability of any future modeling. The uncertainty inherent in using the complete distribution of benzene concentrations and velocities increases substantially the increase in expected probability for well impacts. Site-specific, maximum concentrations should be used, as opposed to a generic distribution that assumes no knowledge of the LUFT site.
- Groundwater capture zones should be included in the analysis. This model approach assumes that all plumes move towards a nearby well but with no influence from the well itself. Further probabilistic modeling should be performed to ascertain the sensitivity of this approach to well-capture zones and known groundwater-flow directions.
- More knowledge is required concerning the subsurface environment in California. One
  of the major unknowns in any hydrogeological investigation is the lack of knowledge of
  subsurface geology. A great deal can be learned even from the moderate to poor quality
  of data available in CAL-DWR well logs. This data should be transcribed into electronic
  format for use by researchers attempting to draw conclusions on the subsurface.
- A drinking water well sampling frequency policy that is based on proximity to LUFT sites may be more protective of public water supplies. Public water agencies should consider higher sampling rates for wells that are situated near known LUFT releases, or any other known release, in order to protect public health<sup>12</sup>.
- Further comparative analysis of impacted public drinking water wells to gasoline continuing ethanol or MTBE and well-impacted LUFT sites is needed. Rempel's 1995 report should be updated to help to understand what factors result in well impacts throughout California.
- A voluntary sampling program for private wells should be established by the state of California. In order to protect a portion of the public that currently has no regulatory oversight to protect against well contamination, California should institute a program designed to identify areas where sampling of private wells may be required and offer screening samples to that population.
- Data already collected by various state organizations should be systematically organized for use in decision analysis.

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<sup>&</sup>lt;sup>12</sup> This was a recommendation of the MTBE Blue Ribbon Panel (BRP, 1999) as well.

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#### 8.7. References

- Ang, A.H-S., and W.H. Tang (1975). *Probability Concepts in Engineering Planning and Design, Vol. 1.* John Wiley and Sons, New York, NY.
- Bear, Jacob (1972). Dynamics of Fluids in Porous Media. Elsevier, New York, NY.
- Bear, Jacob (1979). Hydraulics of Ground Water. McGraw-Hill, New York, NY.
- BRP (Blue Ribbon Panel) (1999). Achieving Clean Air and Clean Water; The Report of the Blue Ribbon Panel in Oxygenates in Gasoline. Unit States Environmental Protection Agency, Washington, DC. September.
- California State Senate (1999a). Senate Bill 529 (Bowen) Motor Vehicles Fuels. Available: <a href="http://www.sen.ca.gov/">http://www.sen.ca.gov/</a>>.
- CAL-DHS (California Department of Health Services) (1999a). Water Quality Monitoring (WQM) Database. California Department of Health Services, Sacramento, CA. Accessed: October 1999.
- CAL-DHS (California Department of Health Services) (1999b). Permits, Inspection, Compliance, Monitoring, and Evaluation (PICME) Database. California Department of Health Services, Sacramento, CA. Accessed: October 1999.
- CAL-DWR (California Department of Water Resources) (1997). EXTERRA Database. California Department of Water Resources, Sacramento, CA.
- Cleary, R.W., and M.J. Ungs (1978). *Analytical Models for Groundwater Pollution and Hydrology*. Princeton University, Princeton, NJ. Water Resources Program Report 78-WR-15.
- Dooher, B.P. (1998). Making Risk-Based Management Decisions at Fuel Hydrocarbon Impacted Sites Under Sparse Data Conditions. Ph.D. Dissertation, University of California at Los Angeles, Los Angeles, CA.
- Dooher, B.P., and A.M. Happel (1999). Evaluating the Feasibility of a Statewide Geographic Information System—Design and Testing of an Internet Accessible Geographical Environmental Information Management System. Lawrence Livermore National Laboratory, Livermore, CA. UCRL-AR-134611.
- Giannopoulos, J. (1999). Public Hearing of the State Water Resources Control Board; Testimony on the University of California at Davis MTBE Report. State Water Resources Control Board, Sacramento, CA, February 19.
- Gelhar, L.W., A. Mantoglou, C. Welty, and K.R. Rehfeldt (1985). A Review of Field Scale Subsurface Solute Transport Processes under Saturated and Unsaturated Conditions (Draft Report). Electric Power Research Institute, Groundwater Studies, Palo Alto, CA. EPRI EACCCC.

- Guven, O., F.J. Molz, and J.G. Melville (1984). An analysis of dispersion in a stratified aquifer. *Water Resour. Res.* **20**: 1337-1354.
- Happel, A.M., E.H. Beckenbach, and R.U. Halden (1998). An Evaluation of MTBE Impacts to California Resources. Lawrence Livermore National Laboratory, Livermore, CA. UCRL-AR-130897
- Jury, W.A. (1985). Spatial Variability of Soil Physical Parameters in Solute Migration: A Critical Literature Review. Electric Power Research Institute, Palo Alto, CA, EPRI EA-4228.
- MacKay, D.M., P.V. Roberts, and J.A. Cherry (1985). Transport of organic contaminants in groundwater. *Environ. Sci. Technol.* **19:** 384-392.
- McNab, W.W., D.W. Rice, J. Bear, R. Ragaini, C. Tuckfield, and C. Oldenburg (1999a). *Historical Case Analyses of Chlorinated Volatile Organic Plumes*. Lawrence Livermore National Laboratory, Livermore, CA. UCRL-AR-133361.
- McNab, W., S.E. Heermann, and B. Dooher (1999b). Screening model evaluation of the effects of ethanol on benzene plume lengths. In: *Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate—Report to the California Environmental Policy Council in Response to Executive Order D-5-99. Vol. 4, Potential Ground and Surface Water Impacts, D.W. Rice and G. Cannon (Eds.). Lawrence Livermore National Laboratory, Livermore, CA. UCRL-AR-135949 Vol. 4 Ch. 4.*
- Malcolm Pirnie, Inc. (1998). *Evaluation of the Fate and Transport of Ethanol in the Environment*. Report prepared for American Methanol Institute, Washington, DC. Malcolm Pirnie, Inc., Oakland, CA, November. Report No. 3522-001.
- Molson, J.W., J.F. Barker, and M. Schirmer (1999). *Modeling the Impact of Ethanol on the Persistence of BTEX Compounds in Gasoline Contaminated Groundwater*. California MTBE Research Partnership, Waterloo, Canada. NWRI-99-DRAFT. November.
- (OCWD) Orange County Water District. (1999). Well Description Database. Orange County Water District, CA. Accessed:
- Rempel, R. (1995). Review of available data from sites reported in LUSTIS database as having affected a water supply well. State Water Resources Control Board Memorandum. August.
- Rempel, R., H. Temko, and K. McGee (1996). *California Leaking Underground Fuel Tank* (*LUFT*) *Historical Case Analyses: Data Collection, Data Input, and Data Quality Control.* Contaminated Soils and Groundwater Conference, Association for the Environmental Health of Soils, Newport Beach, CA, March 11–14.
- Schirmer, M, J.W. Molson, and J.F. Barker (1999). The potential impact of alcohol as a gasoline oxygenate on BTEX degradation at spill sites. *Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water*. National Ground Water Association, Houston, TX, Nov. 17–19, 1999. National Ground Water Association, Westerville, Ohio.
- SCVWD (Santa Clara Valley Water District) (1999). *FELIX and Water Resources Management Databases*. Santa Clara Valley Water District, Santa Clara, CA. Accessed: Senate Bill 989 (1999).

- SWRCB (State Water Resources Control Board). (1989). Leaking Underground Fuel Tank Field Manual: Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure. State Water Resources Control Board, Sacramento, CA.
- SWRCB (State Water Resources Control Board). (1999). *Leaking Underground Fuel Tank Information System (LUSTIS) Database*. State Water Resources Control Board, Sacramento, CA. 3<sup>rd</sup> Quarter.
- Ulrich, G. (1999). *The Fate and Transport of Ethanol-blended Gasoline in the Environment*. Governors' Ethanol Coalition, Lincoln, NE. October.
- US Census (United States Bureau of the Census) (1992a). *Census of Population and Housing,* 1990: Summary Tape File 3 on CD-ROM (California) (machine-readable data files). Prepared, produced, and distributed by the U.S. Bureau of the Census, Washington, DC.
- US Census (United States Bureau of the Census) (1992b). *Census of Population and Housing,* 1990: Summary Tape File 3 on CD-ROM Technical Documentation. Prepared by the U.S. Bureau of the Census, Washington, DC.
- van Genuchten, M.T., and W.J. Alves (1982). *Analytical Solutions of the One-dimensional Convective-dispersive Solute Transport Equation*. United States Department of Agriculture, Washington, DC. Technical Bulletin 1661.
- Wexler, E.J. (1992). Analytical Solutions for One-, Two-, and Three-dimensional Solute Transport in Groundwater Systems with Uniform Flow. U.S. Geological Survey, Washington, DC. USGS TWRI 3-B7.
- Wilson, J.L., and P.J. Miller (1978). Two-dimensional plume in uniform groundwater flow. *ASCE Journal of the Hydraulic Division* **104**: 503–514.

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## Figures

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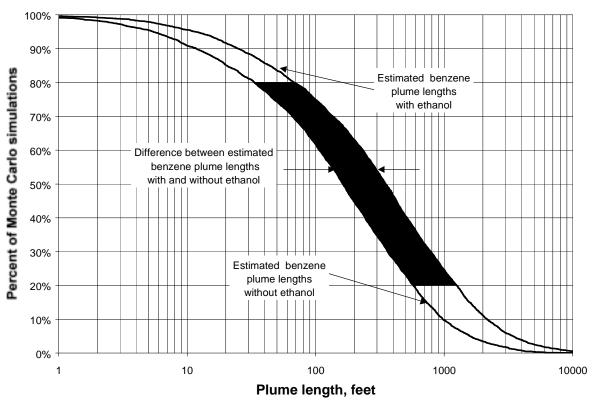


Figure 8-1. Example of the derivation of the multiplier used in this analysis.

# Monte Carlo analysis with *Cleary and Ungs* (1978) model

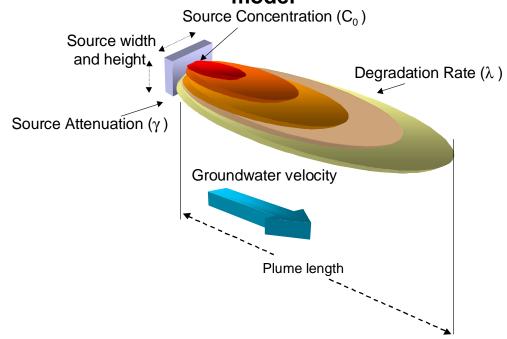


Figure 8-2. Conceptualization of the three-dimensional plume.

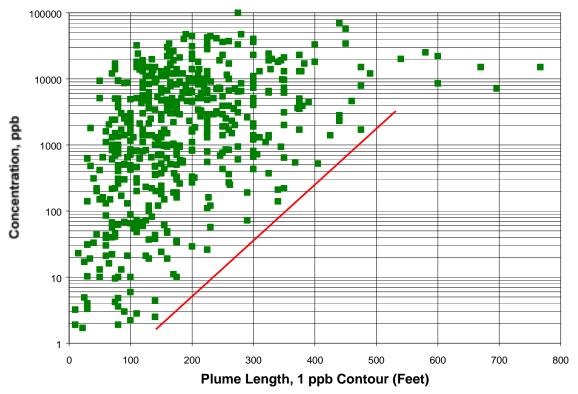


Figure 8-3. Best Professional Judgement benzene plume length vs. maximum benzene concentration.

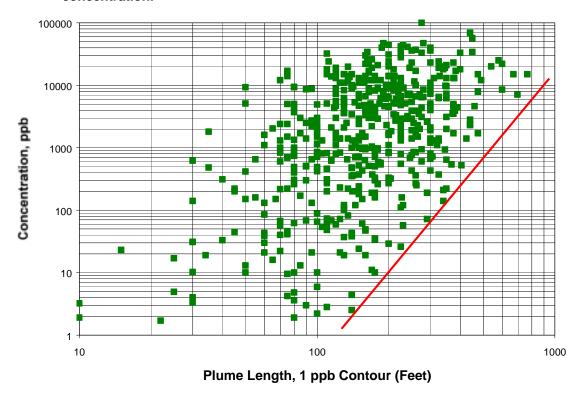


Figure 8-4. Best Professional Judgement plume length vs. maximum concentrations (log-log scale).

Comparison of BPJ Plumes, Non-Parametric Plumes, and 3-D MC Plume Distributions

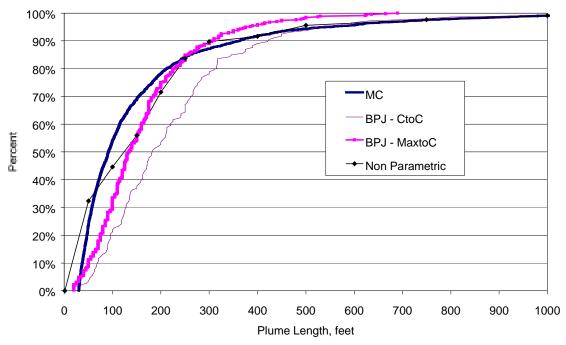


Figure 8-5. Comparison of 3-D Monte Carlo simulated plumes with nonparametric and Best Professional Judgement derived plumes.

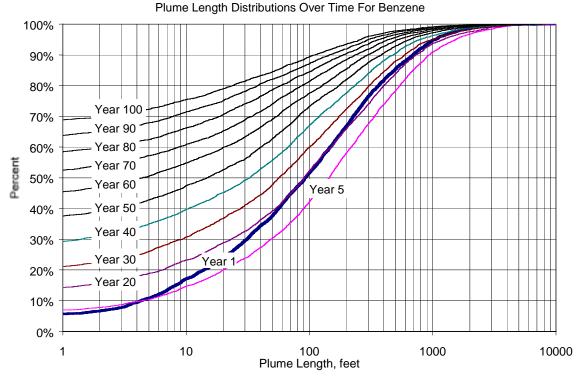


Figure 8-6. Cumulative distributions of benzene plume length over time.

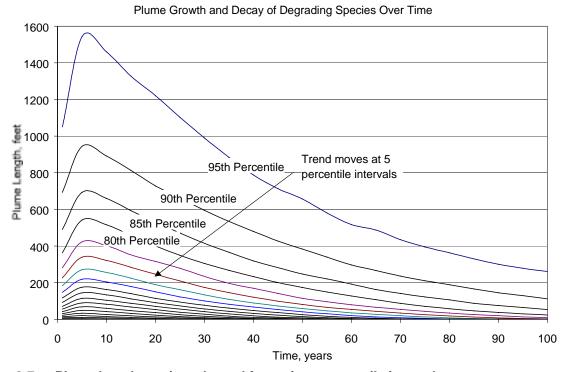


Figure 8-7. Plume length vs. time elapsed for various percentile intervals.

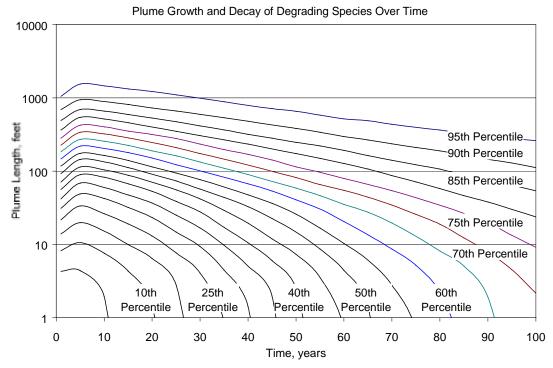


Figure 8-8. Log scale plume length vs. time elapsed for various percentile intervals.

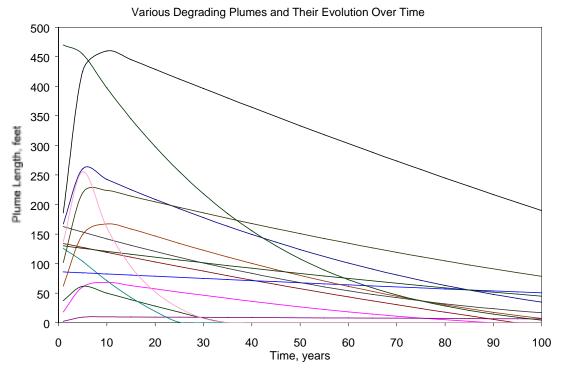


Figure 8-9. Plume length vs. time elapsed for randomly generated plumes.

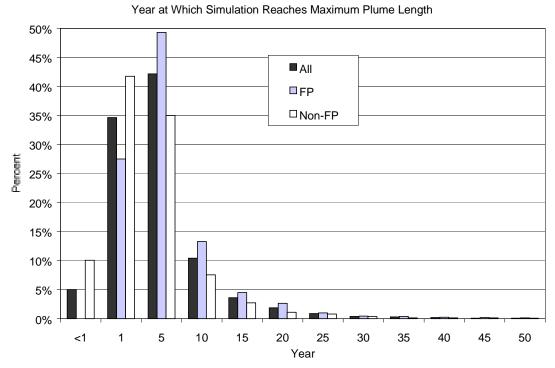


Figure 8-10. Time at which degrading plume reaches its maximum length.

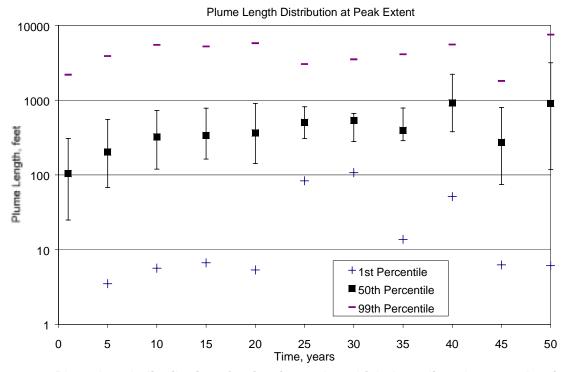


Figure 8-11. Plume length distributions for time interval at which degrading plume reaches its maximum length.

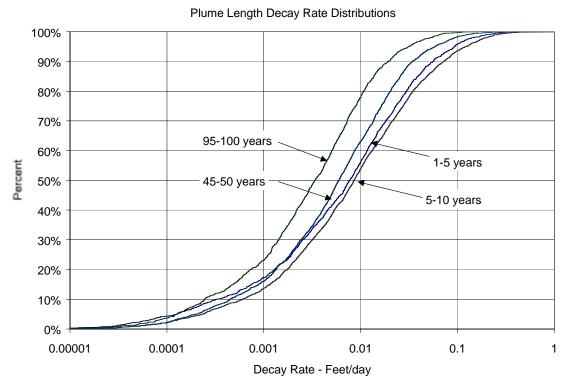


Figure 8-12. Distribution of plume decay rate at various time intervals.

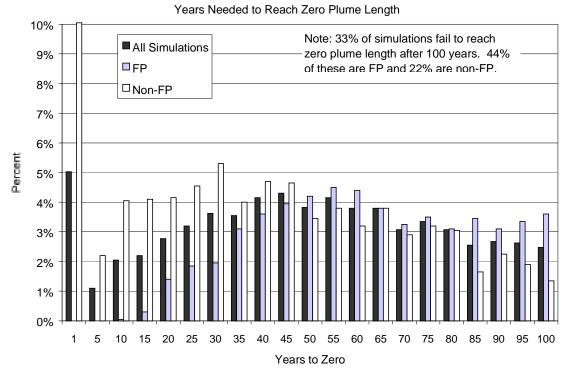


Figure 8-13. Years required for plumes to reach zero plume length.

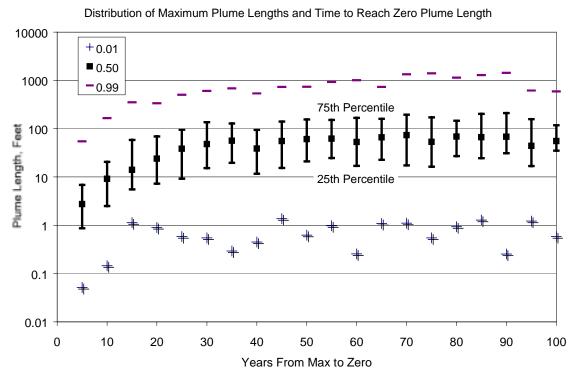


Figure 8-14. Maximum plume length distributions for time interval necessary for plume length to reach zero.

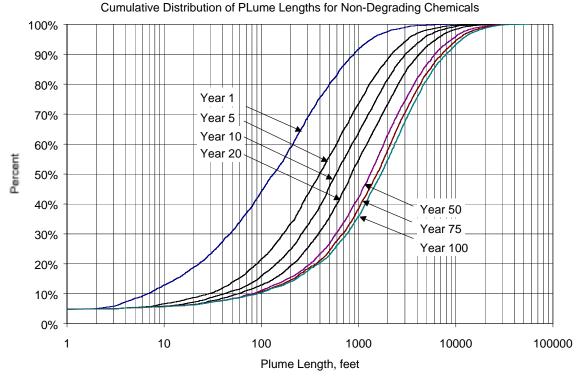


Figure 8-15. Plume length distributions for nondegrading plumes.

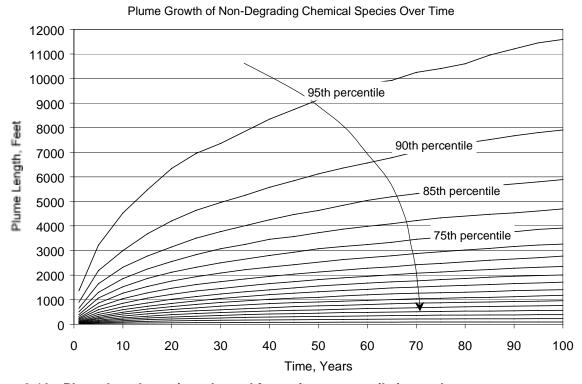


Figure 8-16. Plume length vs. time elapsed for various percentile intervals.

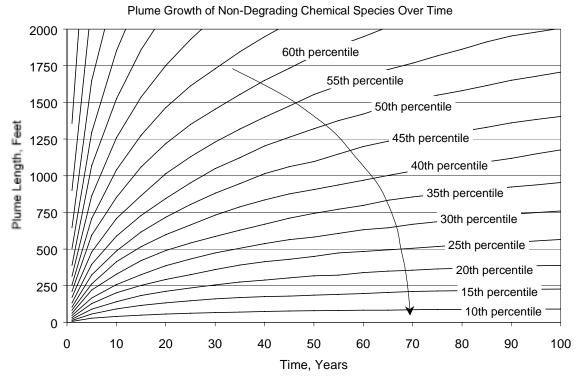


Figure 8-17. Plume length vs. time elapsed for various percentile intervals.

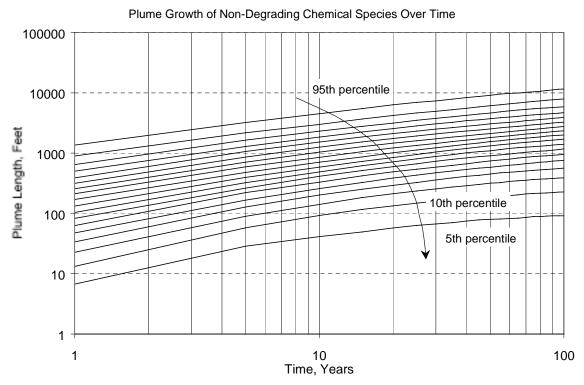


Figure 8-18. Log plume length vs. log time elapsed for various percentile intervals.

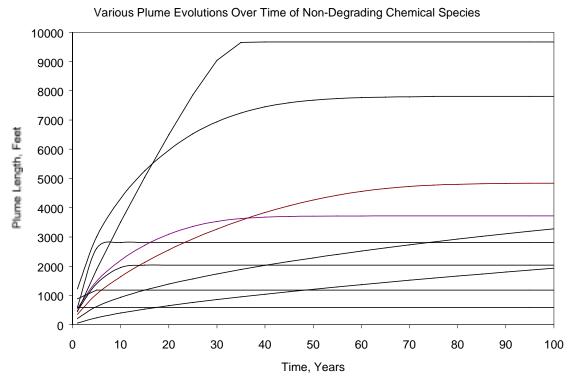


Figure 8-19. Plume length vs. time elapsed for randomly generated plumes.

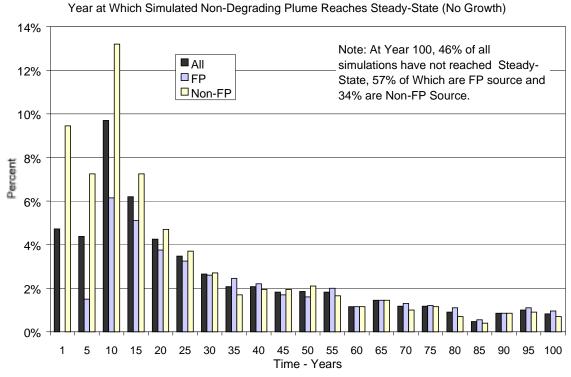


Figure 8-20. Year at which simulated nondegrading plumes reach steady-state.

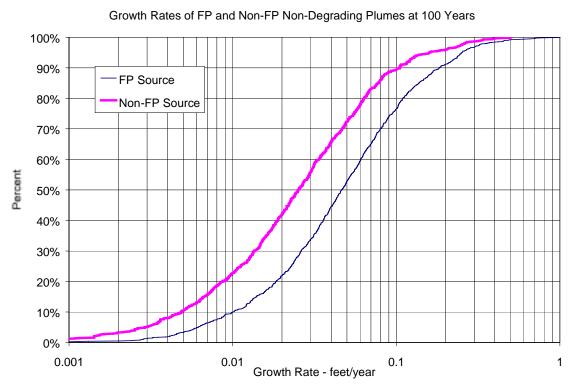


Figure 8-21. Growth rates of free-product and non-free-product plumes at 100 years.

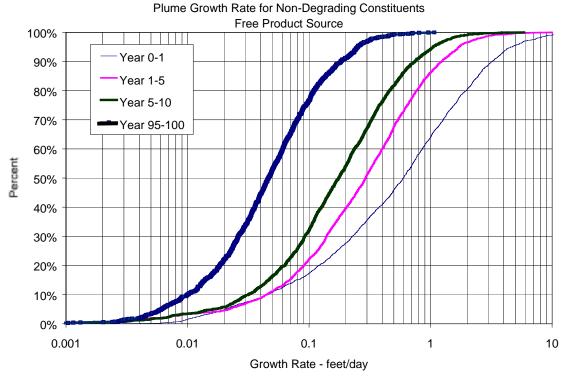


Figure 8-22. Growth rates of free-product plumes over time.

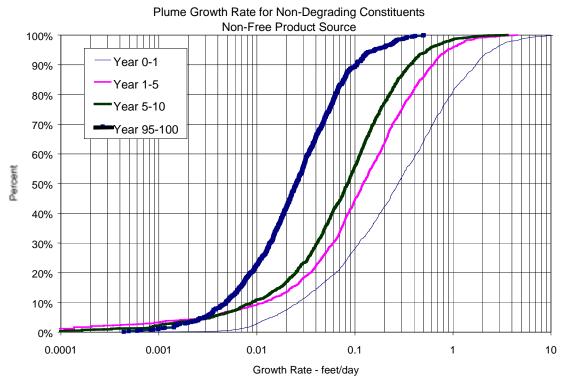
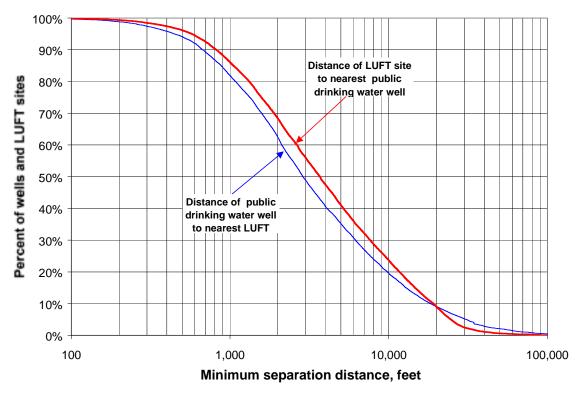


Figure 8-23. Growth rates of non-free-product pumes over time.



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Figure 8-24. Distance of drinking water wells and LUFT sites from each other.

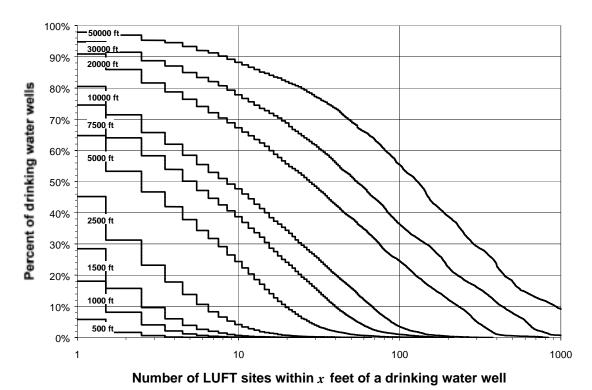


Figure 8-25. Distribution of the number of LUFT sites within x feet of a drinking water well.

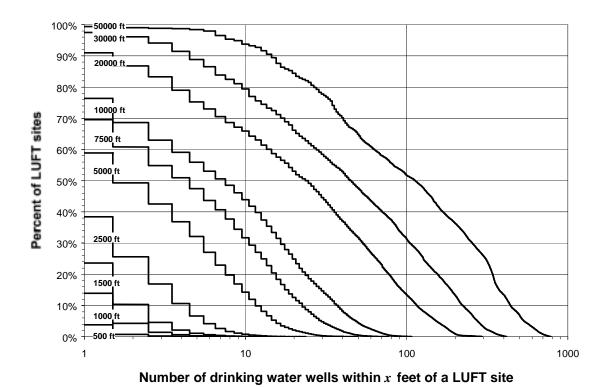


Figure 8-26. Distribution of the number of drinking water wells within x feet of a LUFT site.

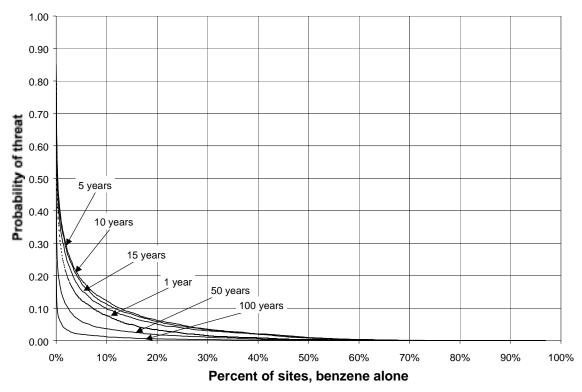


Figure 8-27. Distribution of the absolute probability of threat for LUFT sites with benzene alone.

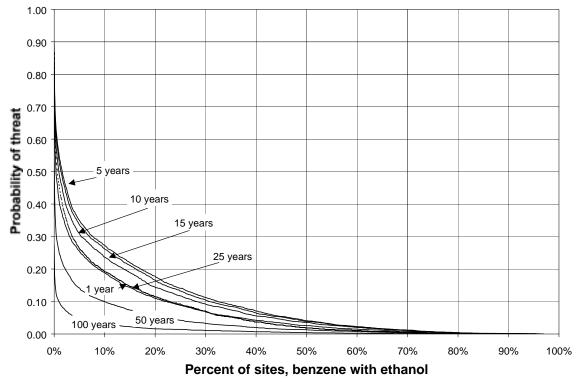


Figure 8-28. Distribution of the absolute probability of threat for LUFT sites with benzene and ethanol.

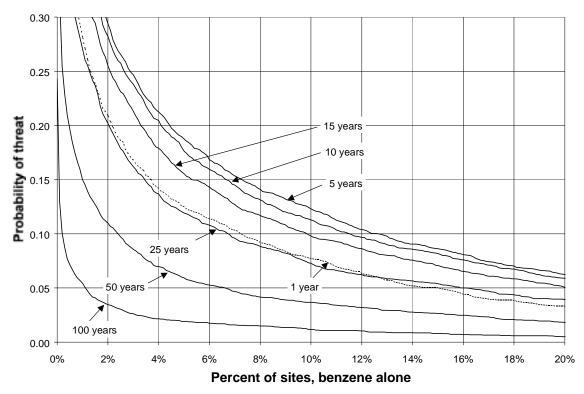


Figure 8-29. Close view of the distribution of the absolute probability of threat for LUFT sites with benzene alone.

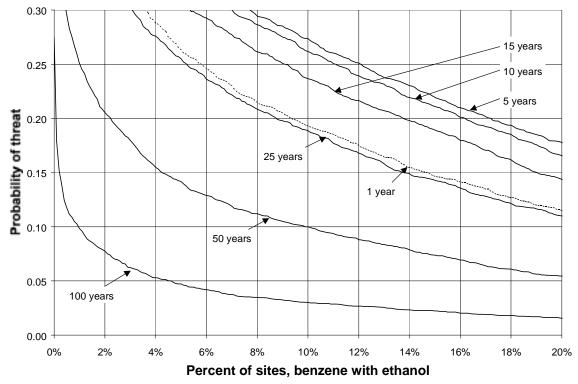


Figure 8-30. Close view of the distribution of the absolute probability of threat for LUFT sites with benzene and ethanol.

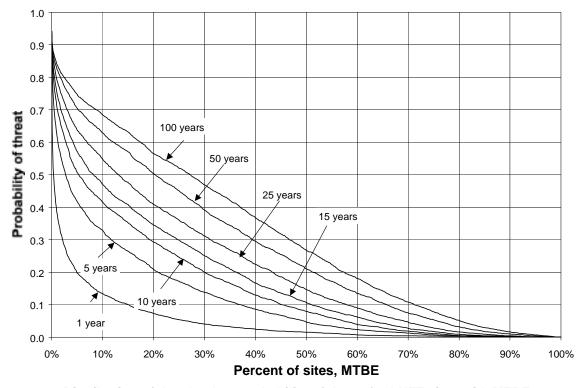


Figure 8-31. Distribution of the absolute probability of threat for LUFT sites with MTBE.

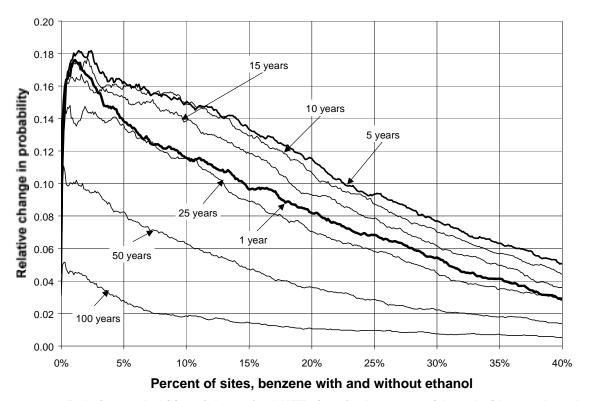
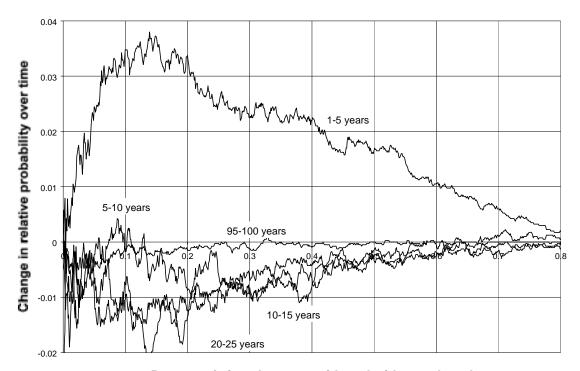


Figure 8-32. Relative probability of threat for LUFT sites for benzene with and without ethanol.



Percent of sites, benzene with and without ethanol

Figure 8-33. Temporal relative change in probability of threat for LUFT sites for benzene with and without ethanol.

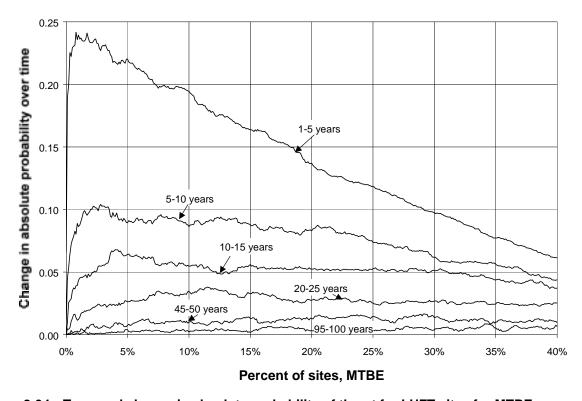


Figure 8-34. Temporal change in absolute probability of threat for LUFT sites for MTBE.

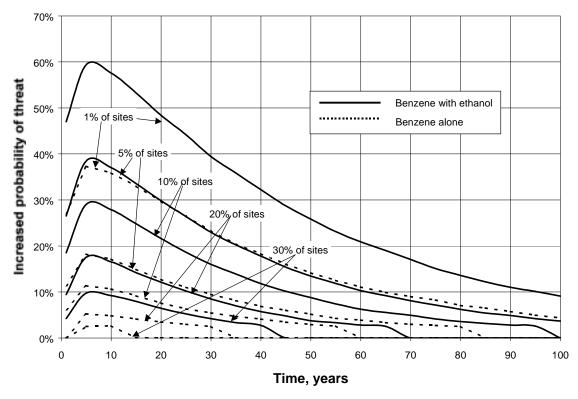


Figure 8-35. Absolute probability of a site threatening any well using de Morgan's law, benzene and benzene with ethanol.

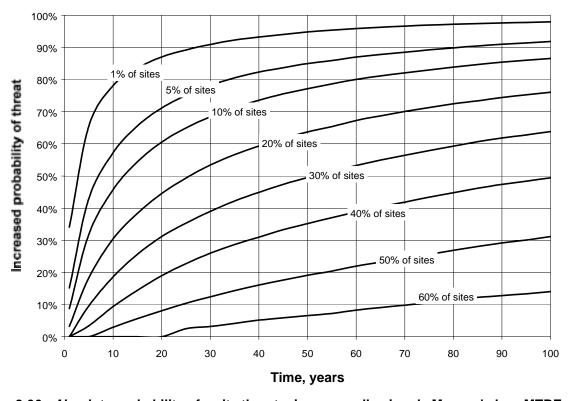


Figure 8-36. Absolute probability of a site threatening any well using de Morgan's law, MTBE.

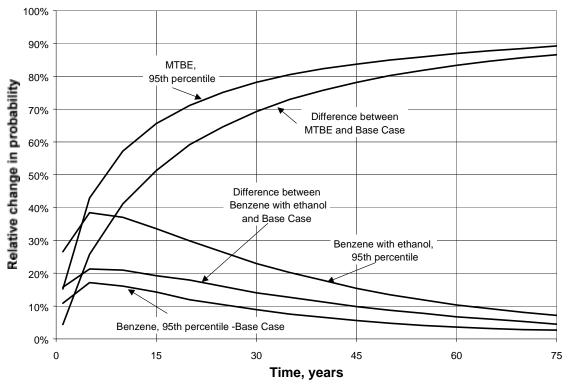


Figure 8-37. Relative probability of a site impacting any well using de Morgan's law.

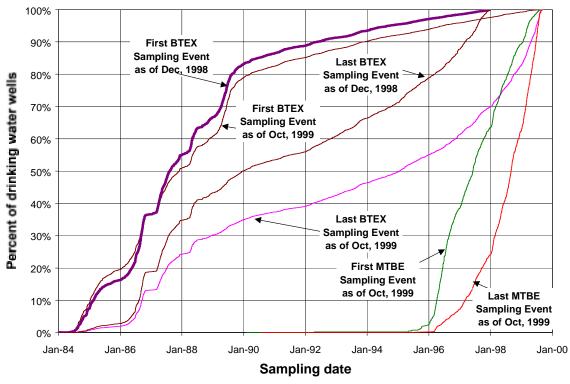


Figure 8-38. First and last sampling event dates for BTEX and MTBE in drinking water wells.

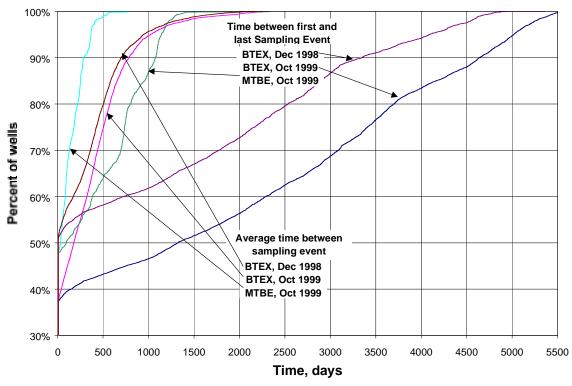


Figure 8-39. Time between first and last sample event and the average time between sample events.

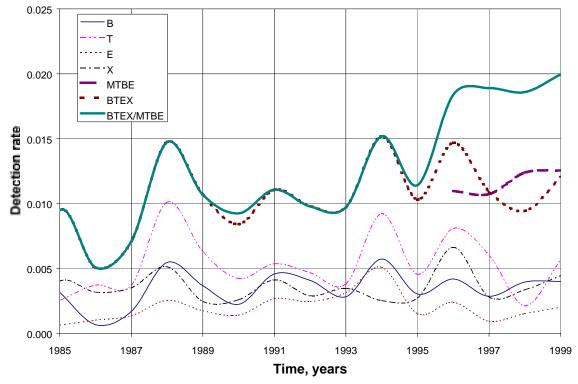


Figure 8-40. Rate of detetections per year of BTEX and MTBE in California public drinking water sources.

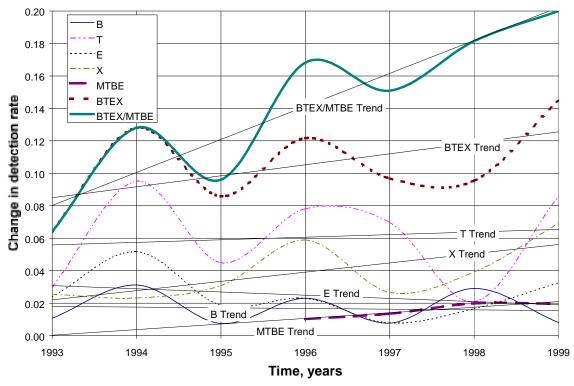


Figure 8-41. Change in detetection rate per year of BTEX and MTBE in California public drinking water sources.

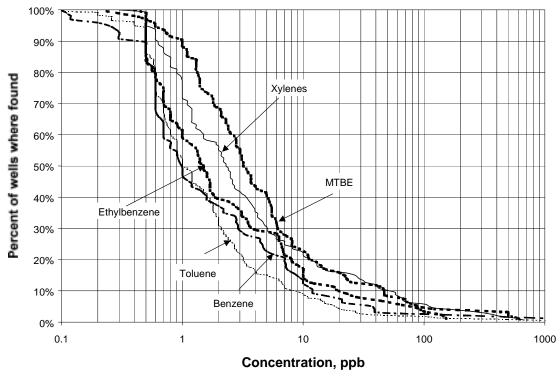


Figure 8-42. Complementary cumulative distribution of BTEX and MTBE detections at impacted drinking water wells in California.

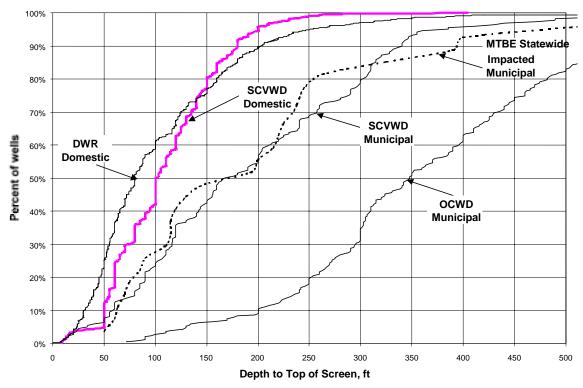


Figure 8-43. Cumulative distribution of depth to top of screen for various public and private drinking water wells in California.

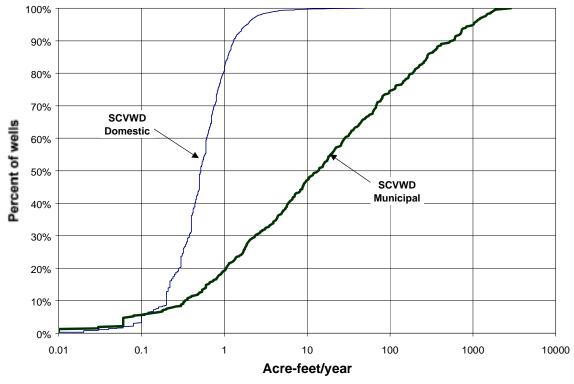


Figure 8-44. Cumulative distribution of well yield for public and private drinking water wells.

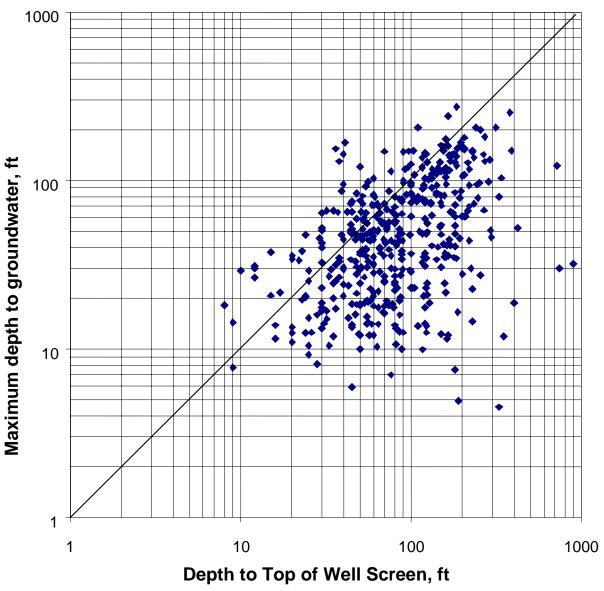


Figure 8-45. Correlation of top of screen interval to maximum groundwater depth for private wells.

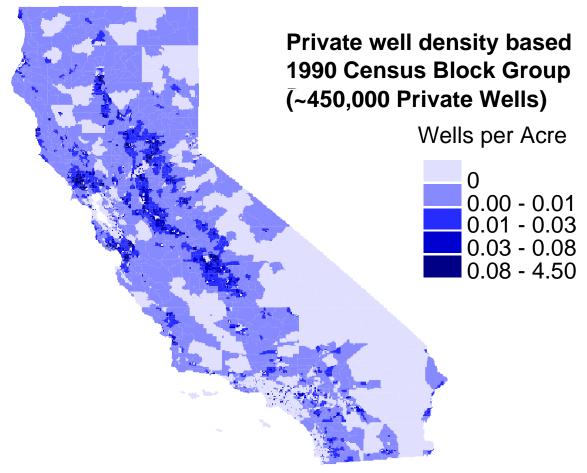


Figure 8-46. Drinking water well density in California (private wells). Darker areas indicate higher densities.

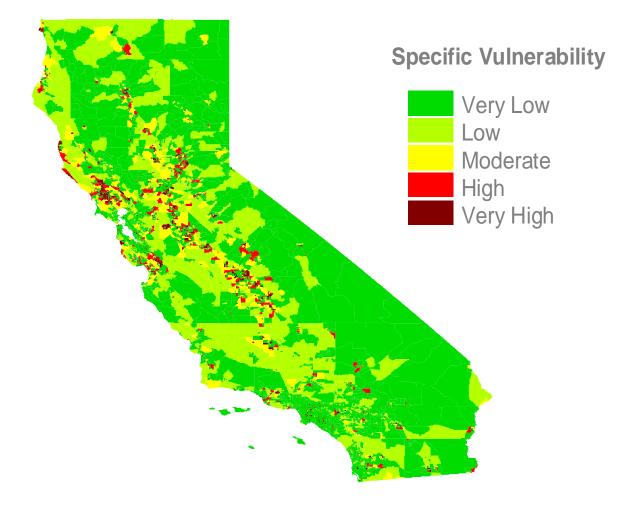


Figure 8-47. Specific vulnerability to private drinking water wells in California at the block group level. Darker areas indicate higher densities of LUFT sites and private wells.

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## Tables

Table 8-1. Notation of Parameters Used in Cleary and Ungs (1978) Equation.

Symbol	Notation Description
C	Concentration
$C_{ m P}$	Maximum or Peak Concentration of Gaussian Source
$D_{\mathrm{x}}$	Dispersion coefficient in the x (longitudinal) direction
$D_{\scriptscriptstyle \mathrm{y}}$	Dispersion coefficient in the y (horizontal) direction
$D_{\mathrm{z}}$	Dispersion coefficient in the z (vertical) direction
$f_{ m oc}$	Organic carbon content of soil
$k_{ m oc}$	Partition coefficient of chemical
R	Retardation
t	Time
$v_{\mathrm{x}}$	velocity component, x direction
$v_{ m y}$	velocity component, y direction
$v_{\mathrm{z}}$	velocity component, z direction
x	Distance in the x direction
у	Distance in the y direction
$Y_0$	Center location of Gaussian source in the y direction
z.	Distance in the z direction
$Z_{0}$	Center location of Gaussian source in the z direction
L	Dispersivity coefficient in the x (longitudinal) direction
Н	Dispersivity coefficient in the y (horizontal) direction
v	Dispersivity coefficient in the z (vertical) direction
	Dummy integration variable
	First order decay/growth coefficient for an exponential boundary source
	Porosity
	First order decay constant for the plume
b	Bulk density of soil
	Correlation coefficient of the source
y	Standard deviation of the Gaussian Source in the y direction
z	Standard deviation of the Gaussian Source in the z direction

**Table 8-2. Population Input Parameters for Monte Carlo Forecasts.** 

Parameter	Description	Remarks	Prescribed distribution
t	Elapsed time since source initiation	Captures a range of typical ages encountered at LUFT sites.	Lognormal distribution.  5th percentile = 730 days (2 years)  mean = 3260 days (8.9 years)  95th percentile = 14,600 days (40 years)
у	Source width	Captures a range of possible release types, from small LUFT tank and pipeline leaks to releases from large industrial facilities. Mean is based on typical $10,000$ -gal tank length. Assumed to correlate with elapsed time, $R = +0.75$ .	Lognormal distribution.  5th percentile = 1.9 m  mean = 10.7 m  95th percentile = 29.6 m
	Source depletion rate (first-order)	Pseudo-first-order decay coefficient which accounts for volatilization, engineered source removal, and other mechanisms of source depletion (Dooher, 1998).	Lognormal distribution. 5th percentile = $7.35 \times 10^{-5}$ day <sup>-1</sup> ( $t_{1/2}$ = 9,420 days or 25.8 years) mean = $2.78 \times 10^{-4}$ day <sup>-1</sup> ( $t_{1/2}$ = 2500 days or 6.8 years) 95th percentile = $6.67 \times 10^{-4}$ day <sup>-1</sup> ( $t_{1/2}$ = 1040 days or 2.8 years)
C <sub>0FP</sub>	Maximum concentration associated with free product sites (38.2% of sites)	Results of MC forecasts are raised to the power of 10 and divided by 1000 (Dooher, 1998). $C_{0FP} = \frac{10^{-\left(20.05,6.84,5.55\right)}}{1000}$	Beta Distribution. a = 20.05 b = 6.84 scale = 5.55
$C_{0L}$	Maximum concentration associated with sites where FP is detected (61.8% of sites)	Results of MC forecasts are raised to the power of 10 and divided by 1000 (Dooher, 1998). $C_{0L} = \frac{10^{T} \left(-0.48, 3.93, 5.09\right)}{1000}$	Triangular Distribution  Minimum = -0.48  Likeliest = 3.93  Maximum = 5.09
K	Hydraulic conductivity	Values typifying California hydrogeology (Dooher, 1998). Values supported by by Mackay <i>et al.</i> (1985) and Guven <i>et al.</i> (1984).	Lognormal distribution. $5^{th}$ percentile = $3.82 \times 10^{-6}$ m/s (0.33 m/day) mean = $1.25 \times 10^{-4}$ m/s (10.8 m/day) $95^{th}$ percentile = $4.75 \times 10^{-4}$ m/s (41 m/day)
h	Hydraulic gradient	Values typifying California hydrogeology (Dooher, 1998). Values supported by by Mackay <i>et al.</i> (1985) and Guven <i>et al.</i> (1984).	Lognormal distribution. $5^{th}$ percentile = $1.42 \times 10^{-3}$ mean = $1.66 \times 10^{-2}$ $9^{th}$ percentile = $5.58 \times 10^{-2}$

**Table 8-2. Population Input Parameters for Monte Carlo Forecasts (continued).** 

Parameter	Description	Remarks	Prescribed distribution
	Porosity	Based on 252 samples taken at the Lawrence Livermore National Laboratory Superfund Site (Dooher, 1998) and Jury (1985).	Normal distribution. $mean = 0.42$ $standard deviation = 0.07$
<sub>x</sub> :L ratio	Ratio of longitudinal dispersivity to plume length	Based on results presented in Gelhar <i>et al.</i> (1992) fitted to the equation $_{x} = 1.022 \left(logL\right)^{3.1179} 10^{N(0,0.7)}$	Normal distribution. mean = 0.0 standard deviation = 0.74
<sub>y</sub> :L ratio	Ratio of horizontal transverse dispersivity to plume length	Based on results presented in Gelhar <i>et al.</i> (1992) fitted to the equation $y = 0.017L^{0.75269}10^{N(0,0.8)}$	Normal distribution. $mean = 0.0$ $standard\ deviation = 0.80$
	First-order degradation rate	Median value may be fairly typical as a macroscopic average for many sites (e.g., Buscheck <i>et al.</i> , 1996).	Lognormal distribution. 5th percentile = $4.62 \times 10^{-4}$ day <sup>-1</sup> ( $t_{1/2}$ = 1500 days or 4.1 years) mean = $9.47 \times 10^{-3}$ day <sup>-1</sup> ( $t_{1/2}$ = 73.2 days or 0.20 year) 95th percentile = $3.47 \times 10^{-2}$ day <sup>-1</sup> ( $t_{1/2}$ = 20 days or 0.055 year)
$f_{oc}$	Fractional organic carbon content	Based on 278 samples taken at the Lawrence Livermore National Laboratory Superfund Site (Dooher, 1998).	Lognormal distribution. 5th percentile = $1.37 \times 10^{-4}$ mean = $1.4 \times 10^{-3}$ 95th percentile = $4.6 \times 10^{-3}$
b	Bulk density	Based on 595 samples taken at the Lawrence Livermore National Laboratory Superfund Site (Dooher, 1998).	Normal distribution. $mean = 1.75 \text{ g/cm}^3$ $standard deviation = 0.22 \text{ g/cm}^3$

Table 8-3. Count of sampled public water sources, by year.

YEAR	В	T	E	X	MTBE	BTEX	BTEX/MTBE
1980	1	1	1	1	0	1	1
1981	1	1	1	0	0	1	1
1982	2	2	2	0	0	2	2
1983	0	0	0	0	0	0	0
1984	1,196	1,188	1,188	1,169	0	1,196	1,196
1985	1,580	1,573	1,571	1,486	0	1,580	1,580
1986	2,957	2,950	2,941	2,828	0	2,957	2,957
1987	2,951	2,960	2,949	2,848	0	2,960	2,960
1988	2,375	2,375	2,357	2,334	0	2,375	2,375
1989	5,708	5,710	5,709	5,687	0	5,710	5,710
1990	3,563	3,547	3,561	3,470	3	3,565	3,568
1991	2,619	2,609	2,618	2,421	0	2,619	2,619
1992	3,676	3,635	3,672	3,452	9	3,672	3,681
1993	3,182	3,143	3,188	3,164	0	3,188	3,188
1994	3,141	3,143	3,141	3,160	1	3,160	3,160
1995	3,294	3,292	3,291	3,292	129	3,294	3,326
1996	3,338	3,338	3,337	3,319	2,279	3,338	3,589
1997	3,149	3,147	3,144	3,198	2,888	3,198	3,493
1998	3,285	3,279	3,281	3,266	3,635	3,285	3,982
1999	2,491	2,483	2,488	2,474	2,310	2,491	2,707

Table 8-4. Cumulative count of sampled public water sources, by year.

YEAR	В	T	E	X	MTBE	BTEX	BTEX/MTBE
1980	5	3	4	3	0	5	5
1981	6	4	5	3	0	6	6
1982	8	6	7	3	0	8	8
1983	8	6	7	3	0	8	8
1984	1,202	1,192	1,193	1,172	0	1,202	1,202
1985	2,614	2,601	2,601	2,499	0	2,614	2,614
1986	4,920	4,907	4,904	4,718	0	4,920	4,920
1987	6,857	6,850	6,845	6,687	0	6,857	6,857
1988	8,212	8,201	8,191	8,112	0	8,212	8,212
1989	10,971	10,971	10,962	10,896	0	10,971	10,971
1990	11,533	11,529	11,522	11,459	3	11,533	11,536
1991	11,924	11,917	11,914	11,839	3	11,924	11,927
1992	12,331	12,327	12,324	12,243	12	12,331	12,343
1993	12,706	12,696	12,700	12,635	12	12,706	12,718
1994	12,995	12,980	12,990	12,937	13	12,995	13,007
1995	13,263	13,247	13,258	13,197	142	13,263	13,288
1996	13,567	13,554	13,563	13,486	2,301	13,567	13,609
1997	13,825	13,812	13,820	13,749	3,853	13,825	13,874
1998	14,066	14,051	14,060	14,004	5,418	14,066	14,144
1999	14,190	14,179	14,183	14,134	6,081	14,190	14,274

Table 8-5. Change in count of sampled public water sources, by year.

YEAR	В	T	E	X	MTBE	BTEX	BTEX/MTBE
1980							_
1981	1	1	1	0	0	1	1
1982	2	2	2	0	0	2	2
1983	0	0	0	0	0	0	0
1984	1,194	1,186	1,186	1,169	0	1,194	1,194
1985	1,412	1,409	1,408	1,327	0	1,412	1,412
1986	2,306	2,306	2,303	2,219	0	2,306	2,306
1987	1,937	1,943	1,941	1,969	0	1,937	1,937
1988	1,355	1,351	1,346	1,425	0	1,355	1,355
1989	2,759	2,770	2,771	2,784	0	2,759	2,759
1990	562	558	560	563	3	562	565
1991	391	388	392	380	0	391	391
1992	407	410	410	404	9	407	416
1993	375	369	376	392	0	375	375
1994	289	284	290	302	1	289	289
1995	268	267	268	260	129	268	281
1996	304	307	305	289	2,159	304	321
1997	258	258	257	263	1,552	258	265
1998	241	239	240	255	1,565	241	270
1999	124	128	123	130	663	124	130

Table 8-6. Count of detections in sampled public water sources, by year.

YEAR	В	T	E	X	MTBE	BTEX	BTEX/MTBE
1980	0	0	0	0	0	0	0
1981	0	0	0	0	0	0	0
1982	0	0	0	0	0	0	0
1983	0	0	0	0	0	0	0
1984	0	0	0	1	0	1	1
1985	5	4	1	6	0	15	15
1986	2	11	3	9	0	15	15
1987	5	11	4	10	0	21	21
1988	13	24	6	12	0	35	35
1989	21	36	10	14	0	61	61
1990	8	15	5	9	3	30	33
1991	12	14	7	10	0	29	29
1992	15	17	9	10	0	36	36
1993	9	12	10	11	0	31	31
1994	18	29	16	8	0	48	48
1995	10	15	5	9	4	34	38
1996	14	27	8	22	25	49	66
1997	9	19	3	9	31	35	66
1998	13	7	5	11	45	31	74
1999	10	14	5	11	29	30	54

Table 8-7. Cumulative count of detections in sampled public water sources, by year.

YEAR	В	T	E	X	MTBE	BTEX	BTEX/MTBE
1980	0	0	0	0	0		
1981	0	0	0	0	0		
1982	0	0	0	0	0		
1983	0	0	0	0	0		
1984	0	0	0	1	0	1	1
1985	5	4	1	6	0	15	15
1986	7	15	4	15	0	30	30
1987	12	26	8	25	0	51	51
1988	25	50	14	37	0	85	85
1989	44	84	24	49	0	140	140
1990	48	99	28	57	3	166	169
1991	54	110	34	65	3	187	190
1992	65	125	42	73	3	218	221
1993	69	136	51	83	3	242	245
1994	78	163	66	90	3	279	282
1995	80	175	71	98	7	302	309
1996	87	199	78	115	29	339	363
1997	89	217	80	122	50	364	403
1998	96	222	84	132	81	387	452
1999	97	233	88	141	94	405	478

Table 8-8. Change in count of detections in sampled public water sources, by year.

YEAR	В	T	E	X	MTBE	BTEX	BTEX/MTBE
1980							
1981	0	0	0	0	0	0	0
1982	0	0	0	0	0	0	0
1983	0	0	0	0	0	0	0
1984	0	0	0	1	0	1	1
1985	5	4	1	5	0	14	14
1986	2	11	3	9	0	15	15
1987	5	11	4	10	0	21	21
1988	13	24	6	12	0	34	34
1989	19	34	10	12	0	55	55
1990	4	15	4	8	3	26	29
1991	6	11	6	8	0	21	21
1992	11	15	8	8	0	31	31
1993	4	11	9	10	0	24	24
1994	9	27	15	7	0	37	37
1995	2	12	5	8	4	23	27
1996	7	24	7	17	22	37	54
1997	2	18	2	7	21	25	40
1998	7	5	4	10	31	23	49
1999	1	11	4	9	13	18	26

Table 8-9. Yearly public water source detection rate.

YEAR	В	T	E	X	MTBE	BTEX	BTEX/MTBE
1980							
1981							
1982							
1983							
1984				0.00086		0.00084	0.00084
1985	0.00316	0.00254	0.00064	0.00404		0.00949	0.00949
1986	0.00068	0.00373	0.00102	0.00318		0.00507	0.00507
1987	0.00169	0.00372	0.00136	0.00351		0.00709	0.00709
1988	0.00547	0.01011	0.00255	0.00514		0.01474	0.01474
1989	0.00368	0.00630	0.00175	0.00246		0.01068	0.01068
1990	0.00225	0.00423	0.00140	0.00259		0.00842	0.00925
1991	0.00458	0.00537	0.00267	0.00413		0.01107	0.01107
1992	0.00408	0.00468	0.00245	0.00290		0.00980	0.00978
1993	0.00283	0.00382	0.00314	0.00348		0.00972	0.00972
1994	0.00573	0.00923	0.00509	0.00253		0.01519	0.01519
1995	0.00304	0.00456	0.00152	0.00273	0.03101	0.01032	0.01143
1996	0.00419	0.00809	0.00240	0.00663	0.01097	0.01468	0.01839
1997	0.00286	0.00604	0.00095	0.00281	0.01073	0.01094	0.01889
1998	0.00396	0.00213	0.00152	0.00337	0.01238	0.00944	0.01858
1999	0.00401	0.00564	0.00201	0.00445	0.01255	0.01204	0.01995
Average	0.00348	0.00534	0.00203	0.00360	0.01553	0.01149	0.01745

Table 8-10. Yearly public water source detection rate, based on cumulative count.

YEAR	В	Т	E	X	MTBE	BTEX	BTEX/MTBE
1980							
1981							
1982							
1983							
1984				0.00085		0.00083	0.00083
1985	0.00191	0.00154	0.00038	0.00240		0.00574	0.00574
1986	0.00142	0.00306	0.00082	0.00318		0.00610	0.00610
1987	0.00175	0.00380	0.00117	0.00374		0.00744	0.00744
1988	0.00304	0.00610	0.00171	0.00456		0.01035	0.01035
1989	0.00401	0.00766	0.00219	0.00450		0.01276	0.01276
1990	0.00416	0.00859	0.00243	0.00497		0.01439	0.01465
1991	0.00453	0.00923	0.00285	0.00549		0.01568	0.01593
1992	0.00527	0.01014	0.00341	0.00596		0.01768	0.01790
1993	0.00543	0.01071	0.00402	0.00657		0.01905	0.01926
1994	0.00600	0.01256	0.00508	0.00696		0.02147	0.02168
1995	0.00603	0.01321	0.00536	0.00743	0.04930	0.02277	0.02325
1996	0.00641	0.01468	0.00575	0.00853	0.01260	0.02499	0.02667
1997	0.00644	0.01571	0.00579	0.00887	0.01298	0.02633	0.02905
1998	0.00682	0.01580	0.00597	0.00943	0.01495	0.02751	0.03196
1999	0.00684	0.01643	0.00620	0.00998	0.01546	0.02854	0.03349
Average	0.00467	0.00995	0.00354	0.00617	0.02106	0.02603	0.02888

Table 8-11. Yearly public water source detection rate, based on count change.

YEAR	В	T	E	X	MTBE	BTEX	BTEX/MTBE
1980							
1981							
1982							
1983							
1984	0.00000	0.00000	0.00000	0.00086		0.00084	0.00084
1985	0.00354	0.00284	0.00071	0.00377		0.00992	0.00992
1986	0.00087	0.00477	0.00130	0.00406		0.00650	0.00650
1987	0.00258	0.00566	0.00206	0.00508		0.01084	0.01084
1988	0.00959	0.01776	0.00446	0.00842		0.02509	0.02509
1989	0.00689	0.01227	0.00361	0.00431		0.01993	0.01993
1990	0.00712	0.02688	0.00714	0.01421		0.04626	0.05133
1991	0.01535	0.02835	0.01531	0.02105		0.05371	0.05371
1992	0.02703	0.03659	0.01951	0.01980		0.07617	0.07452
1993	0.01067	0.02981	0.02394	0.02551		0.06400	0.06400
1994	0.03114	0.09507	0.05172	0.02318		0.12803	0.12803
1995	0.00746	0.04494	0.01866	0.03077	0.03101	0.08582	0.09609
1996	0.02303	0.07818	0.02295	0.05882	0.01019	0.12171	0.16822
1997	0.00775	0.06977	0.00778	0.02662	0.01353	0.09690	0.15094
1998	0.02905	0.02092	0.01667	0.03922	0.01981	0.09544	0.18148
1999	0.00806	0.08594	0.03252	0.06923	0.01961	0.14516	0.20000
Average	0.01267	0.03732	0.01522	0.02360	0.01883	0.06570	0.08271

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## Appendix A Cleary and Ungs (1978) 3-D Solution

A-1

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### Appendix A Cleary and Ungs (1978) 3-D Solution

## A-1. Exact Analytical Solutions to the Advection-Dispersion Equation

Exact analytical solutions are available for some simple geometries. These solutions are useful in developing the model of the plume probability domain, as they give approximations that range from extremely conservative and simple (one-dimensional) to much more realistic (three-dimensional). In the following solutions, the initial condition is one in which there is a rate constant , which can apply either to a source growth or attenuation rate.

In the following equations, retardation may be added by dividing the velocity or dispersivity coefficients by R, which is

$$R = 1 + \frac{k_{oc}f_{oc}}{b}$$
 (A-1)

where  $k_{\rm oc}$  is the partition coefficient for the chemical species in question. (Table 8-1 has the symbols for the following equations.)

For a three-dimensional bivariate gaussian distributed boundary source (represented spatially in Figures A-1 and A-2), the change in concentration over time,

$$\frac{C}{t} = D_x \frac{{}^{2}C}{x^{2}} + D_y \frac{{}^{2}C}{y^{2}} + D_z \frac{{}^{2}C}{z^{2}} - v_x \frac{C}{x} - v_y \frac{C}{y} - v_z \frac{C}{z} - C$$
 (A-2)

subject to the boundary and initial conditions,

the equivalent analytical solution is

$$\begin{split} C\left(x,y,z,t\right) &= \frac{C_{p}x_{-y-z}\left(1-\frac{2}{2}\right)}{4\sqrt{D_{x}}} \exp \frac{v_{x}x}{2D_{x}} - t + \frac{v_{z}\left(z-Z_{0}\right)}{2D_{z}} + \frac{\frac{2}{x}\left(1-\frac{2}{2}\right)}{2} \frac{v_{y}}{2D_{y}} + \frac{y-Y_{0}}{\frac{2}{x}\left(1-\frac{2}{2}\right)} \\ &- \frac{\left(y-Y_{0}\right)^{2}}{2\frac{2}{x}\left(1-\frac{2}{2}\right)} \times \sum_{=0}^{\frac{4\sqrt{t}}{3}} \exp \left(-\frac{4\sqrt{t}}{2} - \frac{x^{2}}{4D_{x}}\right) + \frac{\left(z-Z_{0}\right)^{2}}{4D_{z}} + \frac{2\sqrt{t}}{4\sqrt{t}} \\ &\times 2\left(1-\frac{2}{2}\right) + 2D_{z} - \frac{4\sqrt{t}}{2\sqrt{t}} + 2\left(1-\frac{2}{2}\right) + 4D_{y} - \frac{4\sqrt{t}}{2\sqrt{t}} - 8D_{y}D_{z} - \frac{2\sqrt{t}}{2\sqrt{t}} \\ &\times \exp \left(-\frac{4\sqrt{t}}{4D_{y}}\right)^{2} + 2\left(1-\frac{2}{y}\right)^{2} + \frac{y-Y_{0}}{2\sqrt{t}} + \frac{y-Y_{0}}{2\sqrt{t}} + \frac{y-Y_{0}}{2\sqrt{t}} - \frac{y}{2\sqrt{t}} - \frac{y-Y_{0}}{2\sqrt{t}} - \frac{y}{2\sqrt{t}} - \frac{y-Y_{0}}{2\sqrt{t}} - \frac{y-Y_{0$$

$$= \sqrt{\frac{1}{2 \cdot z \left(1 - \frac{2}{z}\right)} + \frac{2D_{y}^{2} \cdot 4}{4D_{y}^{4}} - \frac{2D_{y}^{2} \cdot 4}{z \left(1 - \frac{2}{z}\right) \left(4D_{y}^{4} / + 2 \cdot \frac{2}{y}\left(1 - \frac{2}{z}\right)\right)}}$$
(A-4b)

$$=\frac{\mathbf{v}_{z}}{2D_{z}}-\frac{\left(z-Z_{0}\right)}{2D_{z}^{4}/}-\frac{\left(y-Y_{0}\right)}{\mathbf{y}_{z}\left(1-\frac{2}{z}\right)}+\frac{4D_{y}y^{4}}{\mathbf{z}\left(4Dy^{4}/+2\frac{2}{y}\left(1-\frac{2}{z}\right)\right)}\frac{\mathbf{v}_{y}}{2D_{y}}+\frac{y-Y_{0}}{\mathbf{z}\left(1-\frac{2}{z}\right)}\tag{A-4c}$$

$$= - + \frac{v_x^2}{4D_x} + \frac{v_y^2}{4D_y} + \frac{v_z^2}{4D_z}$$
 (A-4d)

When there is uni-directional flow, the above becomes

$$C(x,y,z,t) = \frac{C_{P}x_{y}z(1-\frac{2}{2})}{4\sqrt{D_{x}}} \exp \frac{v_{x}x}{2D_{x}} - t \int_{=0}^{4\sqrt{t}} \frac{4\sqrt{t}}{3} \exp \left(-\frac{4}{2} - \frac{x^{2}}{4D_{x}}\right) - \frac{(z-Z_{0})^{2}}{4D_{x}} + \frac{2}{4} \frac{2}{2}$$

$$\times \frac{2}{z}(1-\frac{2}{2}) + 2D_{z} - \frac{4}{2} \frac{2}{y}(1-\frac{2}{2}) + 4D_{y} - \frac{4}{2} - 8D_{y}D_{z} - \frac{2}{2} \frac{8}{2} - \frac{1}{2}$$

$$\times \exp \left(-\frac{(y-Y_{0})^{2}}{4D_{y}^{4} + 2\frac{2}{y}(1-\frac{2}{2})}\right) d$$

$$(A-5a)$$

$$= \sqrt{\frac{1}{2 \cdot z \left(1 - \frac{2}{z}\right)} + \frac{1}{4D_{H}^{4}} - \frac{2D_{H}^{2} \cdot 4}{z \left(1 - \frac{2}{z}\right) \left(4D_{H}^{4} / + 2 \cdot \frac{2}{y}\left(1 - \frac{2}{z}\right)\right)}}$$
(A-5b)

$$= \frac{4D_{H} - (y - Y_{0})}{y - z \left(4D_{H} - (y - Y_{0}) + 2 - \frac{2}{y}(1 - y)\right)\left(1 - y - 2\right)} - \frac{(z - Z_{0})}{2D_{V} - (y - Y_{0})} - \frac{(y - Y_{0})}{y - z(1 - y)}$$
(A-5c)

$$= - + \frac{v_x^2}{4D_L} \tag{A-5d}$$

Where  $\alpha$ ,  $\beta$ , and  $\psi$  are temporary variables.

#### A-2. References

Cleary, R.W., and M.J. Ungs (1978). *Analytical Models for Groundwater Pollution and Hydrology*. Princeton University, Princeton, NJ. Water Resources Program Report 78-WR-15.

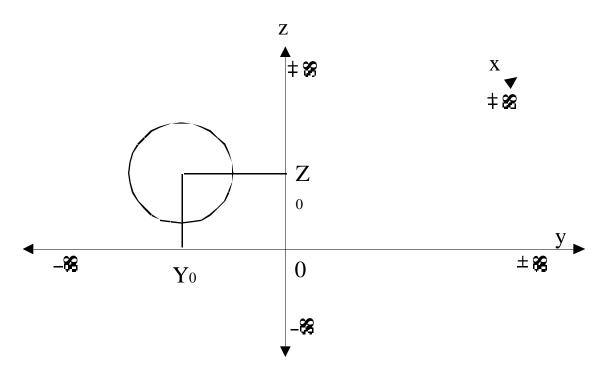


Figure A-1: Bivariate Gaussian source of infinite areal extent for three-dimensional flow.

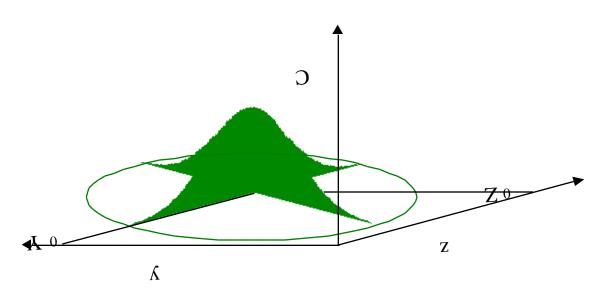


Figure A-2. Bivariate Gaussian source of infinite areal extent for three-dimensional flow – concentration distribution.

Potential Ground and Surface Water Impacts

# Appendix B Results of Public Water Sources throughout California

2-99/Ethanol Ch. 8 B-1

12-99/Ethanol Ch. 8 B-2

# Appendix B Results of Public Water Sources throughout California

Table 8-3 to 8-5 show the yearly count of tested public water sources throughout California. Table 8-3 shows the count of tested water sources by year. Public water sources include public drinking water wells and also surface water sources. Public drinking water wells are the vast majority of sources represented. The use of the results of this testing as part of an evaluation of potential groundwater impacts will yield conservative results because groundwater impacts will be overestimated somewhat.

The BTEX column is the combined count of wells tested for BTEX alone; the BTEX/MTBE is the combined count for BTEX and MTBE. There are a small number of water sources that have not been tested for BTEX, but that have been tested for MTBE. This likely reflects small systems that have been asked to report MTBE testing, but are not required to report BTEX sampling unless there is a detection. Table 8-4 is the year cumulative total of the sampled water sources, and Table 8-5 shows the yearly change in the number of water sources sampled. Tables 8-6 to 8-8 show the same counts for sources reporting BTEX and MTBE detections.

Tables 8-9 to 8-11 combine the above six tables. Table 8-9, also seen as Figure 8-40, shows the yearly detection rate for benzene, toluene, ethylbenzene, total xylenes, MTBE, and the combined count. Figure 8-40 shows a fairly constant pattern of BTEX detections, with a slight upward trend in MTBE. Figure 8-41 looks at the change in these trends on a yearly basis. There is a large upward trend in total xylenes and MTBE, and a small upward trend in toluene detections. Both benzene and ethylbenzene exhibit negative detection trends over time. The upward trend in BTEX detections is driven by the large total xylenes detection trend. The cyclic trend can be partially explained through a cyclic source sampling trend, but the cycling needs to be examined more closely.

12-99/Ethanol Ch. 8 B-3